KINETICS OF MICELLES CATALYZED REACTIONS

DISSERTATION

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By

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CERTIFICATE

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This is to certify that the work described in the dissertation entitled " **Kinetics of micelles catalyzed reactions**" is the original work of the candidate and is suitable for submission for the award of M.Phil degree in chemistry.

(Prof. Firdz Ahmad)
Supervisor

****

DEDICATED

TO MY

PARENTS

A C K N O W L E D G E M E N T

All the thanks are due to almighty Allah, who bestowed upon me the capability necessary to achieve this target.

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[FARHAT HASAN KHAN]

C O N T E N T S
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GENERAL INTRODUCTI(

GENERAL INTRODUCTION

A : General background of Micellar catalysis

There are theoretical as well as practical reasons for the study of kinetics in the presence of micelles. On the practical side, industrial application for carrying out reactions in micellar medium often involves the solubilization of the reactants. On the theoretical side, reactions occuring in or on micelles are of especial interest when ionic reactants are involved because of the large electrostatic contributions to the free energy of activation resulting from the micellar charges. Judging by kinetic data for ionic reactions on monolayers, the electrostatic acceleration or retardation could easily amount to several orders of magnitude[1].

In addition one would expect kinetic 'medium effects' due to short-range interactions between the molecules which form the micelles and the molecules of reactants and transition state complex. These effects are also important.

The biological significance of micellar catalysis was recognized as simple models for enzyme catalysis both from kinetic point of view and the stereochemical and substrate selectivity. According to Romsted[2] there are differences

between micellar and enzyme catalysis. In enzyme catalyzed reactions the substrate concentration is usually of several orders of magnitude larger than the enzyme concentration where as in micellar catalyzed reactions the concentration of atleast one of the reactants is maintained similar to that of the micelles. For higher order reactions this may then lead to a larger change in the relative concentrations of the reactants. As a result, this difference leads to different concentration effects altering the reaction mechanisms. Kinetics of micellar catalysis need not obey the Michaelies-Menten equation which is generally applied to enzyme catalysis.[3]

In general[4-5], there are two distinct factors governing the micellar effect on organic reactions, one is the local concentration of catalysis which is developed by the electrostatic interaction, between micelles and the substrate, and second one is the medium effect on the study of transition states.

The tendency of micellar effects can be explained in terms of two models, the differences between the bulk and micellar values of pk_a's as well as rate constants are explained in terms of a lower dielectric constant of the micellar surface i.e. solvent effect. Micelles of the surfactant catalyze or inhibit chemical reactions by incorporation of a reactant or

reactants on to the micelles where the rate constants and concentration of the reactants differ from those in the bulk solutions[6-8]. Several theories[9-14] of micellar catalysis which quantitatively accept this concentration effect have been proposed by several authors.

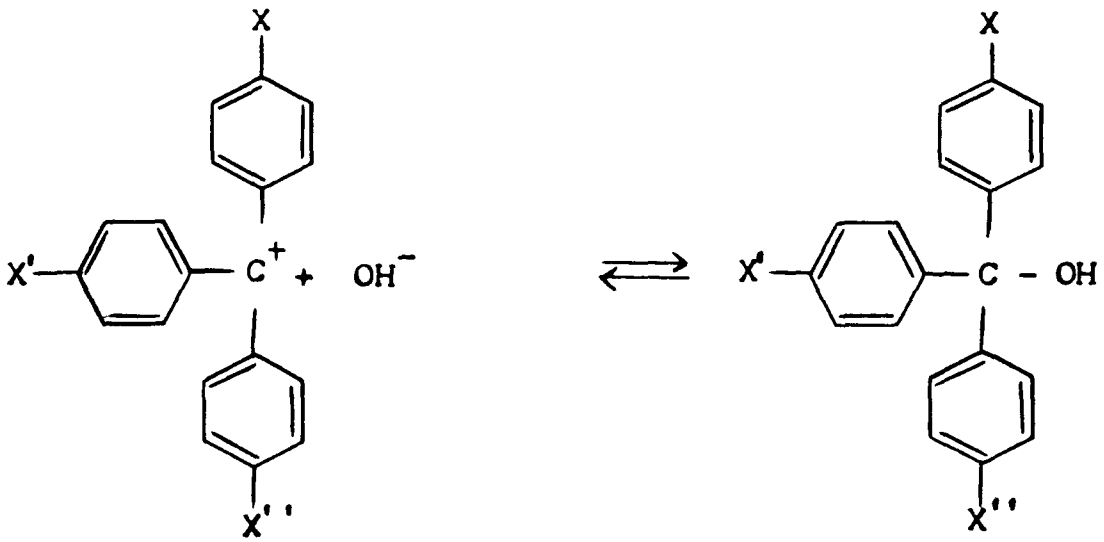
The rate of acceleration or inhibition of organic reactions in micellar solutions arises from different rates of reaction of substrate in micellar phase and in the bulk phase and distribution of the substrate between these two phases. Basically, these effects can be attributed to electrostatic and hydrophobic interactions between the substrate and the surfactant aggregates and in some cases to alterations in the structure of the surrounding water.

The goal of the studies of micellar catalysis is to investigate the substrate specificity and the degree of rate enhancement as well as the other factors which influence the rate and the magnitude of the catalysis.

Recently Hafiane[15] has examined the degrees of association of hydrogen, lithium, rubidium, cesium, cupric and chromic ions to anionic micelles of sodium dodecyl sulphate by ultrafiltration technique. It has been observed that small monovalent cations exhibit no specific adsorption whereas large monovalent cations or multivalent cations are strongly rejected by ultra-

filtration membrane exhibiting specific adsorption on the micelle surface. As pointed out by a group of workers[16,17] ultrafiltration is a valuable tool for studying the distribution of ions between the bulk solution and the micelle surface.

Duynstee and Grunwald[1] have studied the rate of fading of triphenylmethane dyes and of sulfonaphtholein indicators in alkaline solution in the presence of micelle-forming detergent salts. They have reported that the rate of fading of R^+ is greatly accelerated by the addition of the cationic detergent (CTAB) and is greatly retarded by the anionic detergent sodium lauryl sulfate.



Forward reaction (fading)

Blokhus and Sjoblom[18] have studied the adsorption of sodium dodecyl sulphate and benzyl alcohol onto solid Al_2O_3 from aqueous solutions at varying concentration of NaCl. They have observed that adsorption of both SDS and BzOH was found to increase with increasing solubility. They tried to involve this model system sodium dodecyl-sulphate (SDS)/benzyl alcohol (BzOH)/water at different solubility levels with relevance to offshore condition.

Ige and Soriyan[19] have investigated the inhibition of the aquation of $Fe(Me\ phen)_3^{2+}$ by sodium dodecyl sulphate (SDS) in aqueous acid media and they have proposed a mechanism which explains the pronounced inhibition and pre-micellar activity at low SDS concentration. They have found that the inhibition is due to favourable thermodynamic/hydrophobic/electrostatic binding between the Fe^{II} complex and SDS monomer aggregates.

Dash and others[20] have studied the kinetic of equation and base hydrolysis of a series of cis-(chloro)(amine) bis(ethylene diamine) cobalt (III) carbons in the presence of Triton X-100 and sodium dodecyl sulphate in an aqueous medium. They observed that the values of the ion-exchange equilibrium constant and the relative base hydrolysis rates (k^w/k^m) indicated that both micellar binding and retardation of hydrolysis are governed by hydrophobic and electrostatic interactions.

The kinetics of acid catalysed hydrolysis of methyl, ethyl and butyl acetates in amide, salt and surfactant environments, was studied by Das and Moulik[21]. They have observed that the rate of the acid catalysed hydrolysis of ethyl acetate decreases in the presence of urea and substituted ureas. The amides affect the rate through significant deactivation of the catalyst, whereas the micellar solutions of SDS and CTAB increase the rates of hydrolysis of methyl, ethyl and butyl acetates.

Hansler and Rokita[22] used the kinetic study to compare permanganate oxidation of oligonucleoxides and evaluate the structural basis for the specificity of reaction. The experimental approach contrasts the typical focus on reaction products and contributes as alternative method for determining the dominant reaction of thymine. Most notably their results reveal a strong electrostatic component that controls the modification of poly anionic DNA by anionic oxidant permanganate.

B : Oxidation of amino acids

The kinetics of oxidation of some amino acids in perchloric acid with Cl^- ion as a catalyst at 303°K were studied by Hiremath et al[23] the results were compared with those obtained with chlorine water and HOCl as oxidant. They observed that the results followed identical kinetics being first order with respect to [CBT] and [amino acid] each and fractional order in $[Cl^-]$ $[H^+]$ ions. The variation of ionic strength and addition of the reaction product had no effect on the rate. A mechanisms suitable with the observed kinetics is proposed.

$$SH + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} SH_2^+$$

$$CBT + H^+ \overset{K_2}{\rightleftharpoons} CBTH^+$$

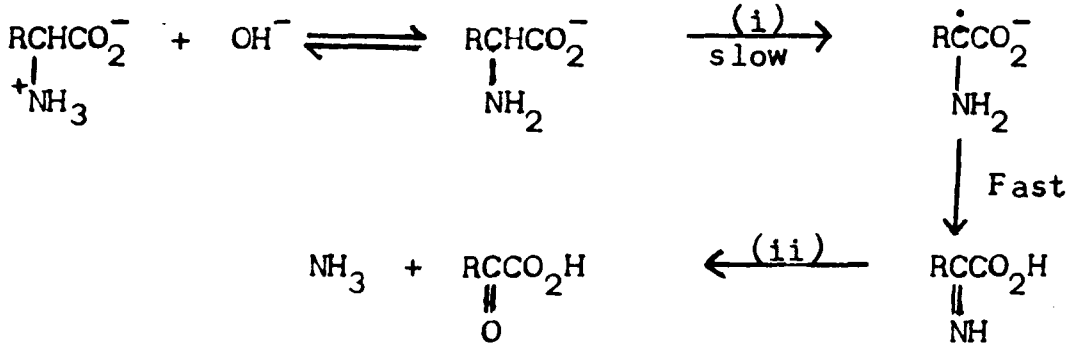
$$CBTH^+ + Cl^- \overset{K_3}{\rightleftharpoons} [C]$$

$$[C] + SH^+ \xrightarrow[\text{slow}]{k} \text{Products}$$

Gowda and Sherigara[24] have investigated the kinetics of oxidation of amino acids by dichloroamine-T (DCT) in 50%(v/v) aqueous acetic acid and 50% (v/v) aqueous methanol media. They observed that in both the media the reaction shows second

order dependence in [DCT] and in the presence of acetate ions in aqueous acetic acid, the reaction is zero order in [amino acid]. The rate increases with the increasing ionic strength of the medium. Furthermore, the authors have investigated effects of changes in solvent composition and the reaction product on the rate in all the cases. They have suggested a suitable mechanistic schemes in confirmity with the observed kinetics features.

The kinetics of oxidation of amino acids by alkaline hexacyanoferrate (III) has been reported at constant ionic strength over the temperature range 318-338 K by Laloo and Mahanti[25]. Their observations show that the rate was dependent on the concentration of the substrate and the oxidant.



The mechanism proposed is a well established path way for the oxidation of amino acids to keto acid via intermediate formation of amino acid.

Panda and Saha[26] have studied the kinetics of N-bromo acetamide (NBA) oxidation of amino acids in the perchloric acid medium at a fixed $Hg(OAc)_2$ concentration they observed that the reaction follows a first order dependence in [NBH] and fractional order in [substrate], the dependence on $[H^+]$ being inverse fractional order. The proposed reaction mechanism scheme is given as,

$$RCH(\overset{+}{N}H_3)COOH \overset{K_1}{\rightleftharpoons} RCH(NH_2)COOH + H^+$$

$$NBA + H_2O \overset{K_2}{\rightleftharpoons} HOBr + \text{Acetamide (ACM)}$$

$$RCH(NH_2)COOH + HOBr \overset{K_3}{\rightleftharpoons} [\text{Complex}]$$

$$[\text{complex}] \xrightarrow[\text{slow}]{k_d} RC^+HNH_2 + CO_2 + H_2OBr^-$$

$$RC^+HNH_2 \xrightarrow{-H^+} RCH{=}NH \xrightarrow{H_2O} RCHO + NH_3$$

Ramachandran et al[27] have studied the kinetics of oxidation of α-amino acids by N-chloro succinimide (NClS) in aqueous media and N-bromosuccinimide (NBS). Analysis of their results show that the observed rate of oxidation is first order in [oxidant] and zero order in [substrate], further perusal of the results indicate that NClS/NBS reacts with α-amino acid anion to produce α-amino acyl hypohalite which then decomposes in the

rate determining step. The mechanism proposed is in accordance with the observed kinetics.

$$>N - X + RCH(NH_2)COO^- \xrightarrow{fast} RCH(NH_2)COOX + >N-$$

X = Cl or Br

$$RCH(NH_2)COOX + OH^- \overset{K_1}{\rightleftharpoons} R - \underset{\displaystyle NH_2}{\overset{\displaystyle H\text{--------}\bar{O}H}{\overset{|}{\underset{|}{C}}}} - COOX$$

$$RCH(NH_2)\dot{C}OOX \xrightarrow{k_1} \text{Products}$$

$$R - \underset{\displaystyle NH_2}{\overset{\displaystyle H\text{-----}\bar{O}H}{\overset{|}{\underset{|}{C}}}} - COOX \xrightarrow{k_2} \text{Products}$$

The kinetics of oxidative degradation of amino acids by peroxodiphosphate (PP) in presence of Ru(III) was studied in detail by Rao[28]. Analysis of the results show that the reaction is found to be acid catalyzed and the dependence of rate on $[H^+]$ reveals that the active oxidizing species is $H_3P_3O_8^-$. The Ru(III) catalysis of PP-AA reaction was explained in terms of formation of a 1:1 complex between Ru(III) and amino acid (AA) which later reacts with PP to give the products.

Yamuna[29] studied the kinetics of oxidation of some amino acids by bromoamine-T (BAT) their observations show a first order dependence each in $[oxidant]_o$, $[amino\ acid]_o$ and inverse first order in $[H^+]$. Added sulphate ions increases the rate while bisulphate ions retarded the reaction. The rate of oxidation increases in the order : leucine > alanine > serine > glycine. The mechanism assumes the interaction of zwitterion of substrate with monobromamine-T in the rate-limiting step. Furthermore, it has been observed that variation of the ionic strength of the medium has no effect on the rate, indicating that neutral species are involved in the rate-determining step. The following proposed mechanism accounts for the observed kinetics :

$$SH^+ \underset{}{\overset{K_1}{\rightleftharpoons}} S^o + H^+$$

$$S^o + RNHBr \xrightarrow[slow]{k_2} X\text{---------}$$

$$X + nRNHBr \xrightarrow{k_3} \text{Products}$$

Ramachandran[30] et al have investigated the oxidation of amino acids in aqueous medium. The results show that the rate of oxidation follows second order with respect to chloramine-T [CAT] and inverse dependence on [P-toluenesulfonamide] : $[RNH_2]$. At constant $[RNH_2]$ the rate expression of the reaction is represented as (in the absence of chloride ion)

$$\frac{-d[CAT]}{dt} = k_a[CAT]^2 + k_b \frac{[Aminoacid][CAT]^2}{[H^+]} + k_c \frac{[Aminoacid][CAT]^2}{[H^+]^2}$$

A linear relationship between pk_1 and the rate constants shows the electrophilic attack of the oxidant at the carboxylate group of amino acid. The mechanism of the reaction has been discussed in terms of the kinetic data.

Gowda and Rao[31-32] have reported the kinetics of oxidative decarboxylation of amino acids by CAT in aqueous perchloric acid medium both in the presence and absence of chloride ions. Their investigations show that in the presence of chloride ion the reaction is first order in $[CAT]_o$. Zero order in $[substrate]_o$ and $[H^+]$ with all the amino acids and second order with $[CAT]_o$. In the absence of chloride ion it follows a first order kinetics in [substrate] and inverse first order on $[H^+]$. At low $[H^+]$ effect of added chloride is not kinetically significant, hence the kinetic features are similar those in the absence of chloride. Plausible mechanism and the rate laws consistent with the mechanism have been reported.

$$SH \overset{K}{\rightleftharpoons} S + H^+$$

$$S + 2RNHCl \xrightarrow{k} S' + 2RNH_2$$

$$S' \longrightarrow \text{Products}$$

the rate law proposed

$$\frac{-d[CAT]}{dt} = k_2[CAT]^2[S]$$

$$= \frac{K_1 k_2 [CAT]^2 [SH]}{[H^+]}$$

C : Role of micelles on the oxidation of amino acids by permanganate

Permanganate has been adopted as a chemical probe with increasing frequency due to its target selectivity depending on the structure of the organic substrate, and depending on the acidity of the medium. The characteristic purple colour of permanganate is due to the tetrahedral permanganate ion, MnO_4^-. It exchanges its oxygen with aqueous solvents rapidly in acid solution but more slowly in neutral and alkaline solutions[33].

Oxidative degradation of amino acids :

Amino acids are the building units of proteins and peptides. These amino acids serve important function in our biological system and play a significant role in metabolism. The kinetic studies of the oxidative degradation of amino acids with different oxidants is receiving great attraction and increasing number of research papers are being produced with remarkable and exciting results. Survey of the current literature shows the way few electron transfer processes have been studied in the presence of surfactant. For the first time Hussain[34] under taken a systematic study of the oxidation of different amino acids to explore the effect of surfactant on the kinetic parameters and mechanistic charges. This is an extension of his work.

Summary of the work in this field is presented below.

Hussain and Ahmad[35] have investigated the effects of SDS (sodium dodecyl sulphate) on the oxidative degradation of isoleucine, their results indicate that the colloidal manganese dioxide is the reduction end product of Mn(VII). The free radical chain reaction involved in the mechanism is retarded in the presence of SDS. The rate passes through a minimum as [SDS] is varied between below and above the cmc. The rate is not affected by $[H^+]$. The overall rate equation proposed is,

$$\frac{-d[Mn(VII)]_{total}}{dt} = \frac{d[Mn(IV)]_{total}}{dt}$$

$$= k_4[ICO_2H]_o[SDS][Mn(VII)]_{total}$$

The stopped-flow[36] technique was used to study the kinetics and mechanism of the oxidation of tryptophane [WCOOH] by acid permanganate in the absence and presence of SDS. The results signify that the reaction is first order with respect of $[MnO_4^-]$ and follows a fraction order with respect to [WCOOH]. However, in the presence of SDS the reaction is first order with respect to $[MnO_4^-]$ and [WCOOH]. The reaction is accelerated by increase in the concentration of hydrogen ion, both in the absence and presence of SDS. The overall rate expression for the reduction

of manganese(VII) is

$$\frac{-d[Mn(VII)]_{total}}{dt} = \frac{k_1[WCOOH]_o[H^+]}{K'+K[H^+]+k_2[WCOOH]_o}[Mn(VII)]_{total}$$

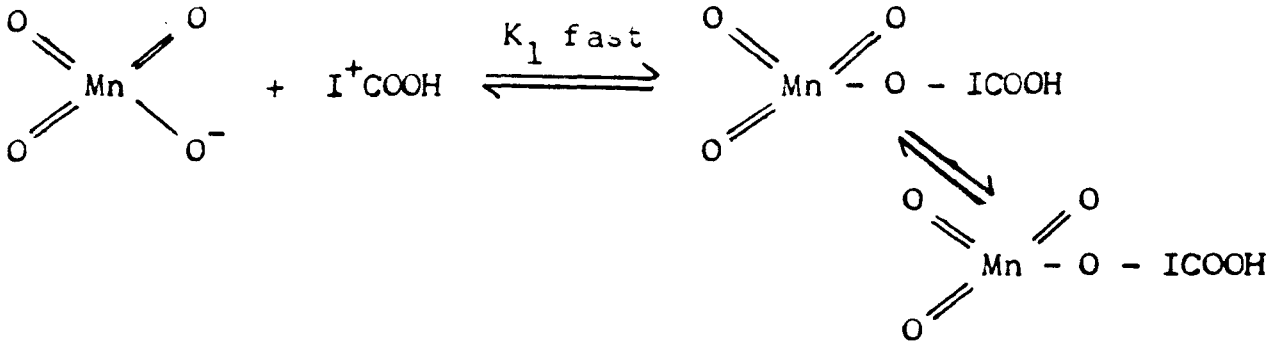
$$\frac{-d[Mn(VII)]_{total}}{dt} = Kk_2'[WCOOH]_o[H^+][SDS][Mn(VII)]_{total}$$

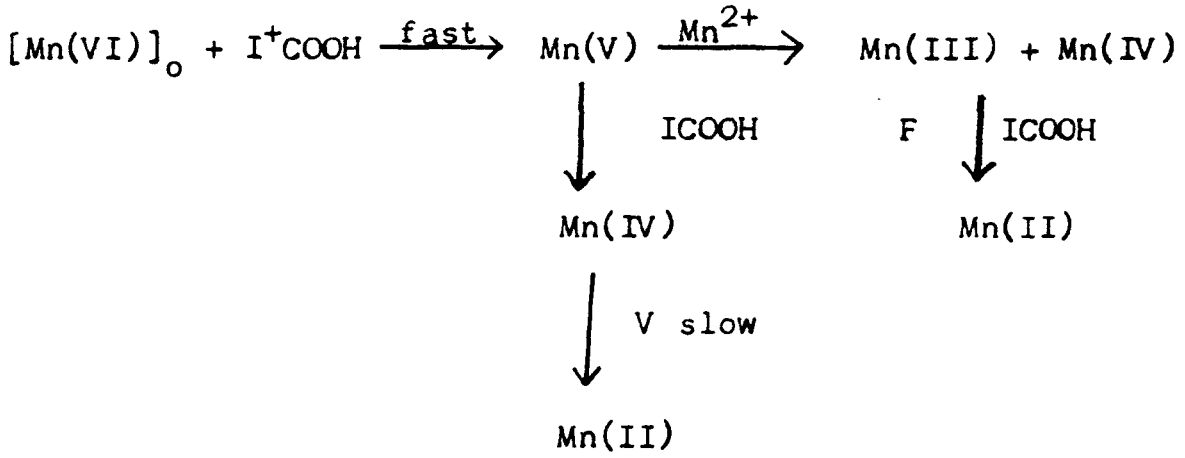
The comperative[37] kinetic study of glutamic acid oxidation in the absence and presence of SDS shows that the surfactant enhances the reaction rate without changing the reaction mechanism. The reaction appears to involve parallel consecutive processes in which Mn(IV) is formed as the reaction intermediate. k_{4f} signifies the rate constant for the path leading to the reduction of Mn(VII) to Mn(II) with prior formation of Mn(IV). The overall rate expression for the reduction of Mn(VII) is

$$\frac{-d[Mn(VII)]_{total}}{dt} = \left\{k_{4f} + k_{2f}/[H^+]\right\}[GCO_2H][Mn(VII)]_{total}$$

The kinetics and mechanism of oxidation of isoleucine by acid permanganate was studied by Husain and Ahmad[38]. The result reported show that the plot between A^{525} vs time increases initially at low concentration of isoleucine, for significant duration, the reported mechanism show that the formation of Mn(IV) is taking place simultaneously by two steps. Mn(IV) and Mn(III) are both produced by the same transient species of Mn(VII).

From the second path it appears that transient species is reacting with amino acid leading to the formations of Mn(IV) only. Thus the fate of Mn(VII) during the course of reaction may be represented as





The overall rate expression reported is

$$\frac{-d[Mn(VII)]_{total}}{dt} = \frac{k[ICOOH]_o}{a+b[H^+]+C[ICOOH]_o}[Mn(VII)]_{total}$$

The kinetics of the oxidative degradation of leucine[39] has been followed spectrophotometrically at 525 nm for the disappearance of Mn(VII) and at 420 nm for the appearance of

Mn(IV). The results signify that the reaction is first order with respect to $[MnO_4^-]$. The rate constant k_7 (for the disappearance of Mn(VII) has been evaluated at different $[LCO_2H]$ and $[H^+]$ and at different temperature from the plot of A_{corr}^{525} vs time. The overall rate satisfying the kinetic parameters is

$$-\frac{1.d[Mn(VII)]_{total}}{[Mn(VII)]_{total}\,dt} = \left\{k'[LCO_2H]_o^{1/2} + k_2'[LCO_2H]_o^2/[H^+]\right\}$$

It is also reported that the decorboxylation involves a cyclic chain reaction.

The oxidation of serine[40] by acid permanganate was investigated both in the absence and presence of SDS. It has been shown that the presence of surfactant enhance the reaction rate. The reaction is first order with respect to [Serine] and $[MnO_4^-]$, the reaction is retarded by $[H^+]$ in the absence of SDS but catalyzed in the presence of SDS. The overall rate expression for the reduction of Mn(VII) is given as

$$-\frac{d[Mn(VII)]_{total}}{dt} = \left\{k_{4f}' + k_{2f}'/[H^+]\right\}\ [Serine]_o[Mn(VII)]_{total}$$

and

$$-\frac{d[Mn(VII)]_{total}}{dt} = \left\{k[H^+] + k'\right\}\ [Serine]_o[SDS][Mn(VII)]_{total}$$

The reaction appears to involve a parallel consecutive reaction mechanism.

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EXPERIMENTAL

MATERIALS

Chemicals used in the kinetic studies of oxidative decaroxylation of lysine in the presence and absence of sodium dodecyl sulphate (SDS) are listed in Table-1, alongwith their respective grades. These reagents were used as received and were of high purity.

Table-1 : List of Reagents

Name	Symbol used	Grade	Supplier
L(+)Lysine	L	AR	BDH (England)
Potassium permanganate	$MnO_4^- \equiv P^-$	AR	Merck-Germany
Perchloric acid		GR	Merck-Germany
Sodium dodecylsulphate	SDS	AR	BDH-England
Sodium perchlorate		AR	BDH-England
Carbon tetrachloride		AR	Merck-India
Silica Gel-TLC		AR	Biogen India
Pyrogallol		AR	Aldrich
Ninhydrin		AR	Koch-light(England)

Purification of sodium dodecyl sulphate :

Sodium dodecyl sulphate (SDS) supplied by (BDH England) was generally used without further purification. To be sure of our results, sodium dodecyl sulphate was further purified[1] 50 gms of SDS was dissolved in 700 ml of 95% alcohol and heated. After filtration and cooling, white blades were obtained, which were again recrystallized from 95% ethanol. The final product was dried in the vacuum desiccator. No significant change appeared in our results. Georges and Chen[2] have also followed the same procedure while studying the catalytic effect of sodium dodecyl sulphate (SDS).

Solution preparation :

Deionized water was used after tripple distillation (the first time from a potassium permanganate solution) as solvent in the experiments. Solutions were prepared immediately before use in water by directly weighing the required quantity. Potassium permanganate solution, however, was prepared and estimated by a standard method[3]. Ionic strength was adjusted by adding sodium perchlorate. Appropriate quantity of sodium dodecyl sulphate (SDS) as solid was dissolved in the substrate solution. These reagents were added as solids so as to maintain a constant volume of the reaction mixture thus avoiding wastage

of the material. The kinetic stuay was made through wide range of amino acid, perchloric acid, sodium perchlorate and sodium dodecyl sulphate concentrations. The concentration of the oxidant was kept constant throughout the kinetic studies, as preliminary experiment showed that change in the concentration of oxidant had no effect on the reaction rate constants.

The studies of different [$NaClO_4$] show that there is no effect of ionic strength on the rate of dissappearance of permanganate ion as well as on the formation of soluble (colloidal) manganese dioxide.

For the analysis of product reaction condition were chosen as far as possible to match the conditions those of the kinetic runs. Acidified solution of the amino acid in large quantity were added to an appropriate volume of potassium permanganate. The solutions were allowed to stand till the reaction mixture became colourless. The reaction mixture was then neutralized by adding an alkali solution drop by drop and simultaneously checking the pH with litmus paper. Then an equal volume of carbon tetrachloride was added to the reaction mixture and the reaction vessel was put on a shaker, the solution was then continuously shaken for 6-8 hours. Subsequently, the whole solution was transferred to a separating funnel and the lower portion was eluted. The extraction from the reaction mixture was done three to four times both in the presence and absence

of SDS. This eluted portion was evaporated at a reduced pressure and was dried completely. The solid substance was collected in air tight bottles. TLC plates were coated with silica-gel - TLC of the extracted product and the corresponding amino acid was run on the same plate. Butanol, acetic acid and water mixture in the ratio of 4:1:5 (by volume) was used as solvent. The plate was taken out and dried in the oven at $40^{o}C$ and kept in the iodine chamber for developing. Only one spot was developed on the plate from the extracted substance and its R_f value was found to be different from the corresponding amino acid. This clearly indicated that the excess of unreacted amino acid was not present in the extracted substance. The single spot of the extracted substance also indicated the purity of the reaction product. This was submitted to IR analysis.

The kinetic studies were also performed in the presence of SDS keeping other conditions same as choosen for the kinetic experiments in the absence of the surfactant. After the completion of the reaction the same process of neutralization was employed as described above. Carbon tetrachloride was used to extract the products of the oxidation in the presence of SDS. Which gave a white precipitate on adding carbon tetrachloride. Rest of the procedure has already been described above. The extracted dry substance was submitted to IR analysis.

IR spectra were obtained with Perkin-Elmer 621 Spectrophotometer (Calibrated with the 1601 cm^{-1} absorption of polystyrene) in CCl_4, in Nujol, or as KBr disk. These IR spectra invariably show the peaks of amines. The presence of ammonia was confirmed by Nessler's reagent, the presence of aldehydes was detected by the usual test[4] as the reaction product. Other workers[5,6] have also reported similar reaction products such as amine, CO_2, ammonia and aldehydes.

Carbondioxide evolved during the oxidation of amino acids in the presence and absence of SDS was measured over dilute sulphuric acid. To make sure that the evolved gas was only carbondioxide, it was passed through different interceptors. No gas could be collected when KOH was used as an interceptor and pyroggallol had no effect. The reaction vessel used for gasometeric purpose consisted of two connected conical flask. In one of the conical flask required reaction mixture was taken and $KMnO_4$ was kept in the other vessel. After allowing for thermal equilibrium to be attained, $KMnO_4$ solution was mixed with the rest by giving a slight till to the reaction vessel.

Unreacted amino acid was quantitatively estimated by using usual Ninhydrin Test and measuring CO_2 evolved. The colorometric measurements were not satisfactory because amine produced also reacted with Ninhydrin.

Identification of free Radicals :

The reaction studies were carried out in the temperature range of 30-40°C. The kinetic runs were done in excess of reductant (i.e. lysine) with respect to oxidant concentration (Permanganate) so that the later could be used as rate monitoring species. Permanganate ion shows a maximum of absorbance at 525 nm (Σ = 2420±10 dm^3 mol^{-1} cm^{-1}) and is almost transparent to radiation at 420 nm (Σ = 29.9±0.2 dm^3 mol^{-1} cm^{-1}). It was also verified that variation in perchloric acid concentration from 0.5 to 0.20 mol dm^{-3} did not significantly change the optical density or the position of maximum absorbance.

The measurements of the optical density of the solution during the kinetic run was done by Bousch and Lomb Spectronic 20 Spectrophotometer.

Generally, the reaction was carried out in glass stoppered corning conical flasks at the required temperature. The temperature was maintained in a thermostated water bath at ±0.1°C of desired value.

Solutions of amino acid, perchloric acid and sodium perchlorate (generally added as solid to maintain the required ionic strength) were taken in the conical flask, an appropriate

volume of potassium permanganate was taken in another flask. The two flasks were kept in the thermostated bath for 15 minutes to bring both the solutions at thermal equilibrium with the bath before starting the kinetic run. Then oxidant was added to the acidified solution of amino acid and mixed throughly by shaking. The reaction was followed by pipetting out 2 ml reaction mixture and adding it to 2 ml ice chilled water so as to slow down the reaction. The rates were determined by monitoring the disappearance of permanganate at 525 nm and by observing the rate of formation of the soluble (colloidal) manganese species at 420 nm. Hussain and Ahmad and others[7-10] have also choosen the same wavelength while studying the permanganate oxidations. All the reactions were followed till atleast 80% of the reaction was (measured in terms of absorbance at 525 nm) completed. The disappearance of yellow colour was attributed to reaction with Mn(IV) and it was also followed at 420 nm.

Keeping the other conditions same as used in the absence of SDS, the required SDS (> cmc >)was added as solid (to maintain the total volume) to the flask containing acidified solutions of amino acid and throughly shaken to dissolve SDS. The flask was kept in a thermostat bath to attain thermal equilibrium at the required temperature. The other flask containing

the solution of potassium permanganate was also allowed to attain the thermal equilibrium in the same bath. Then the two solutions were mixed and the disappearance of permanganate was measured at 525 nm by the usual procedure and the formation of (colloidal) manganese dioxide was measured at 420 nm.

The plot A_{corr}^{530} vs time at high amino acid concentration gave an exponential decay curve.

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MEASUREMENTS AND RATE CONSTANTS

OXIDATION OF LYSINE IN THE ABSENCE OF SDS :

Table 2 + Figure 1a to 1f

Showing effect of the concentration of lysine on the observed rate constant (k_{1ob} and k_{2ob}).

Table-2: Effect of the concentration of lysine on absorbance at 530 nm in the absence of SDS.

Lysine	0.02M	0.04M	0.08M	0.10M	0.12M	0.16M
Time	absorbance at 530 nm					
0	0.520	0.530	0.520	0.520	0.520	0.520
30	0.505	0.510	0.475	0.475	0.460	0.480
60	0.490	0.475	0.435	0.400	0.370	0.380
90	0.480	0.450	0.370	0.340	0.300	0.200
120	0.475	0.420	0.290	0.250	0.240	-
150	0.465	0.380	0.225	0.200	0.185	0.030
180	0.460	0.340	0.170	0.125	0.100	0.010
210	0.445	0.300	0.100	0.080	0.050	0.010
240	0.430	0.260	0.060	0.040	0.025	0.010
270	0.400	0.220	0.030	0.020	0.015	0.010
300	0.370	0.175	0.015	0.015	0.010	
330	0.330	0.135	0.005	0.010	0.010	
360	0.270	0.115	0.005	0.010		
390	0.220	0.100				
420	0.170	0.080				
450	0.115	0.070				
480	0.075	0.060				
510	0.055	0.050				
540	0.045	0.050				
570	0.035					
600	0.025					
630	0.020					
660	0.020					

Temp. = 30°C, $[H^+]$ = 0.20 mol dm^{-3}, μ = 0.20 mol dm^{-3}, $[MnO_4^-]$ = 2×10^{-4} mol dm^{-3}, [SDS] = Nil.

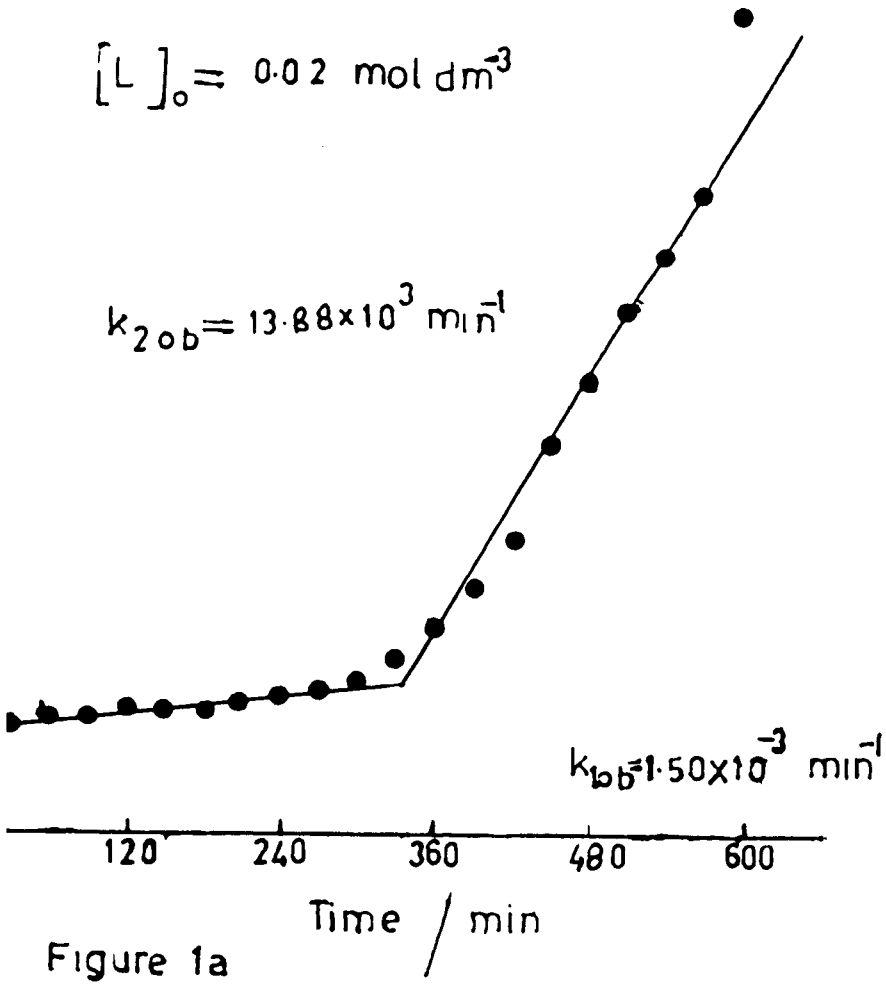


Figure 1a

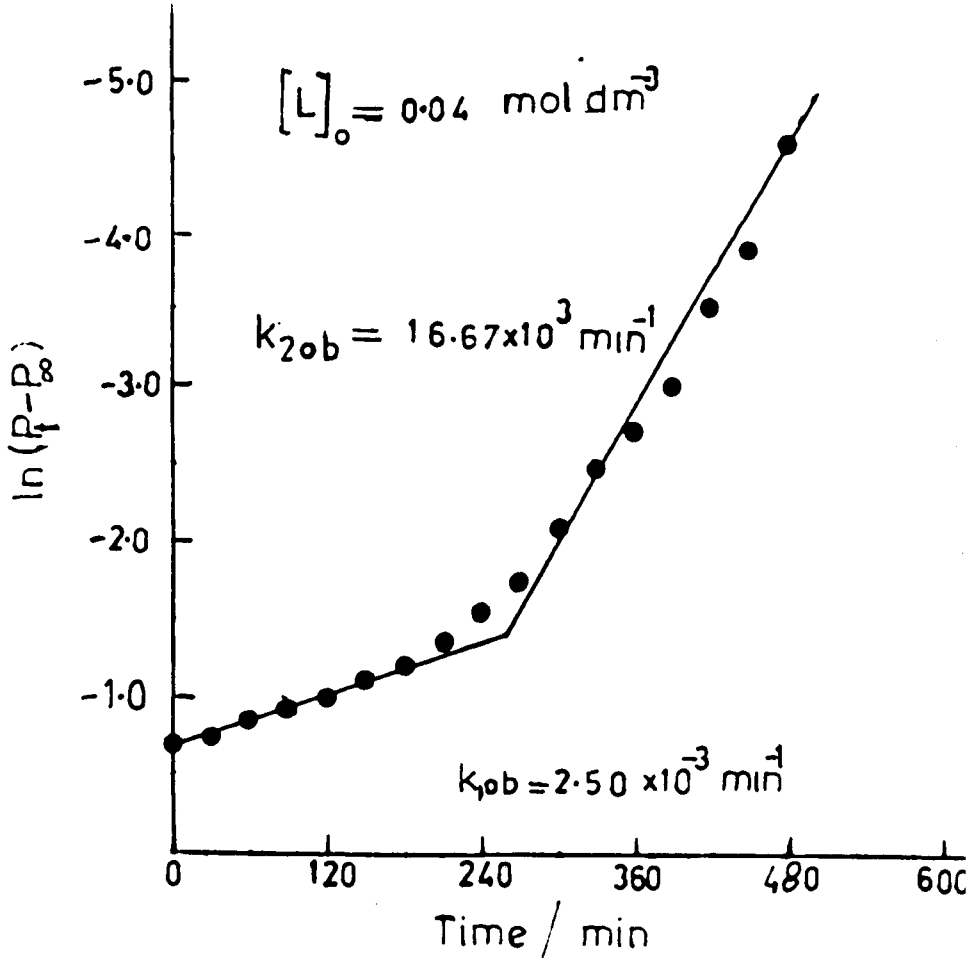


Figure 1b

Plot of ln $(P_t - P_\infty)$ vs time in the absence of SDS
Temp-30°C, $[H^+] = 0{\cdot}20$ mol dm, $\mu = 0{\cdot}20$ mol dm^{-3},
$[MnO_4^-] = 2 \times 10^{-4}$ mol dm^{-3}, [SDS] = Nil

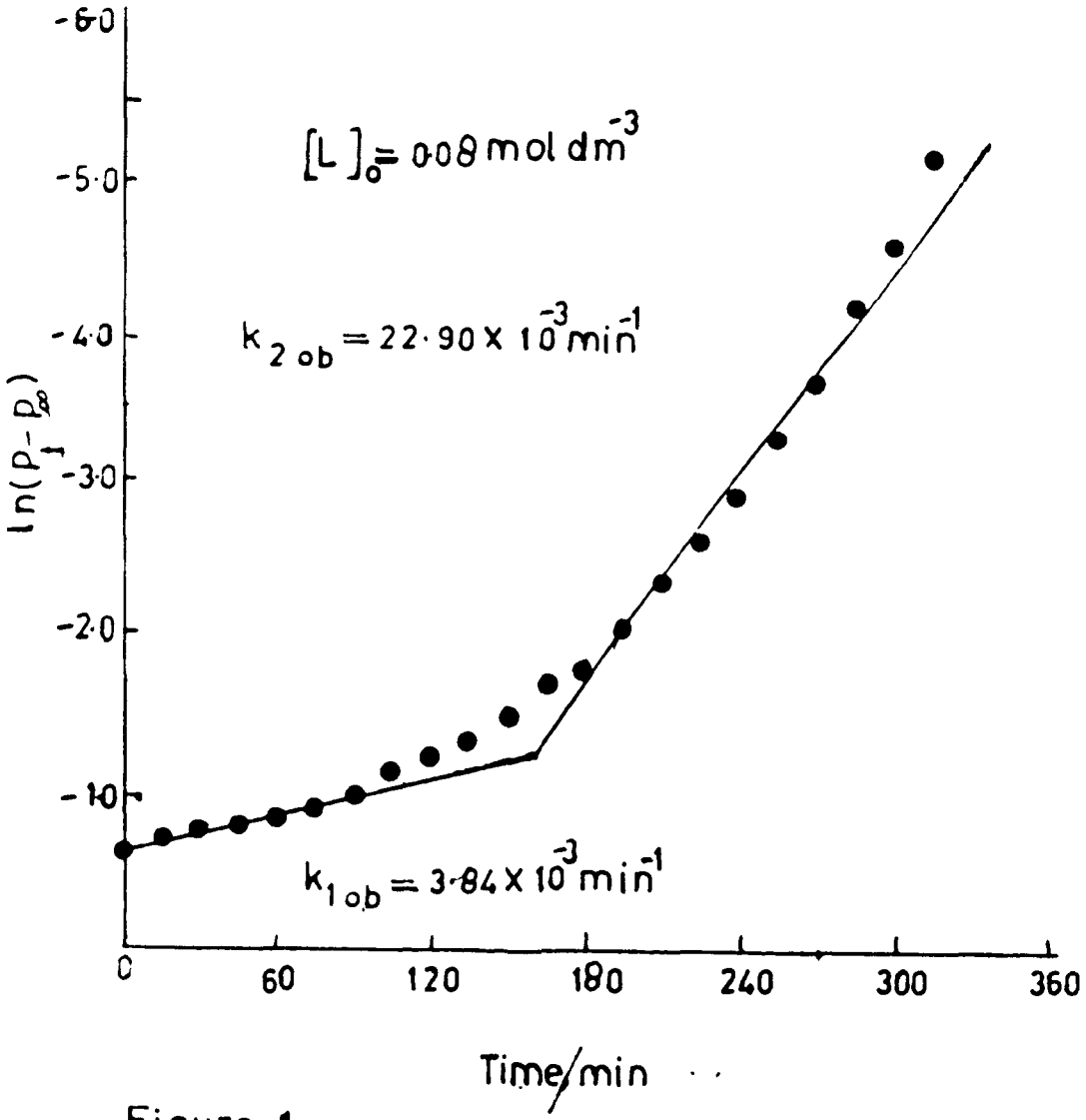


Figure 1c

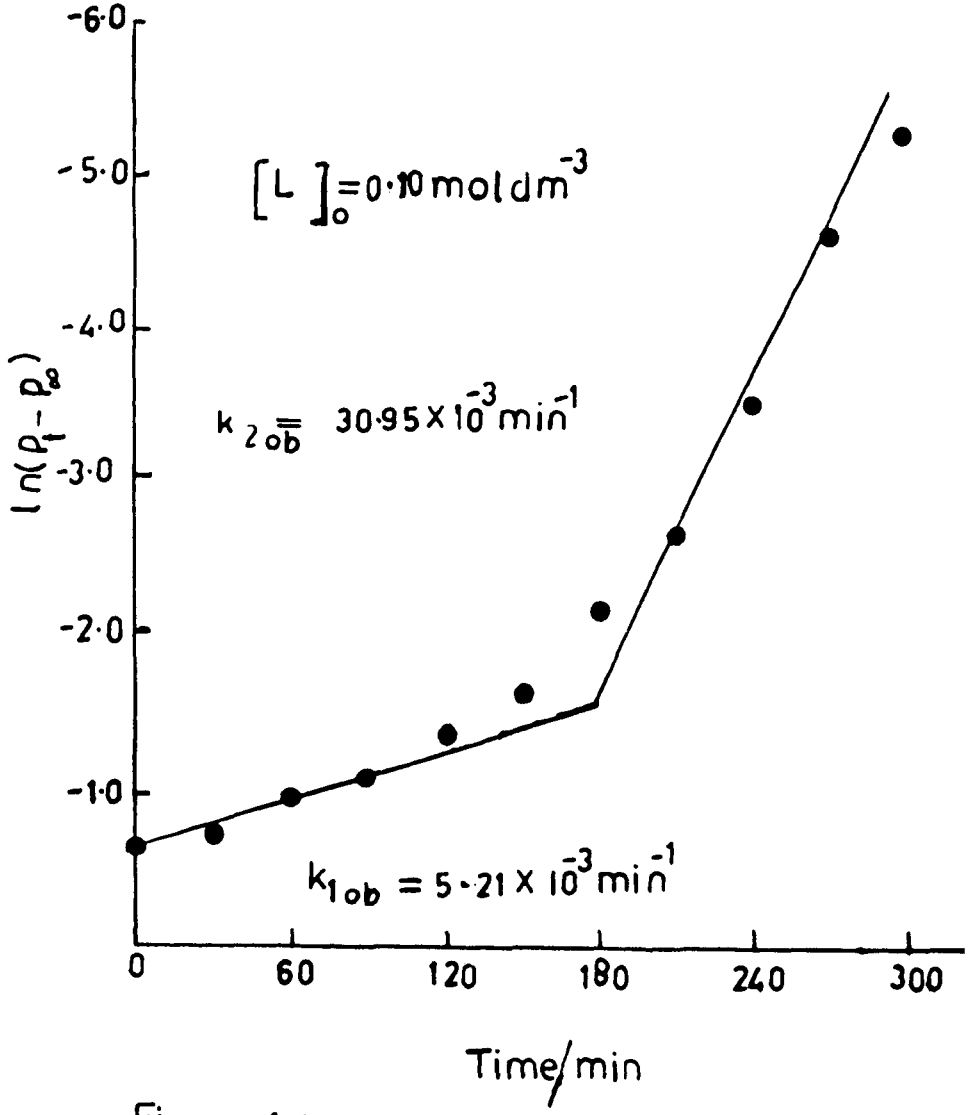


Figure 1d

Plot of ln(P_t P_∞)vstime in the absence of SDS
Temp = 30°C, $[H^+]$ = 0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3},
$[MnO_4^-]$ = 2X10^{-4} mol dm^{-3}, SDS = Nil

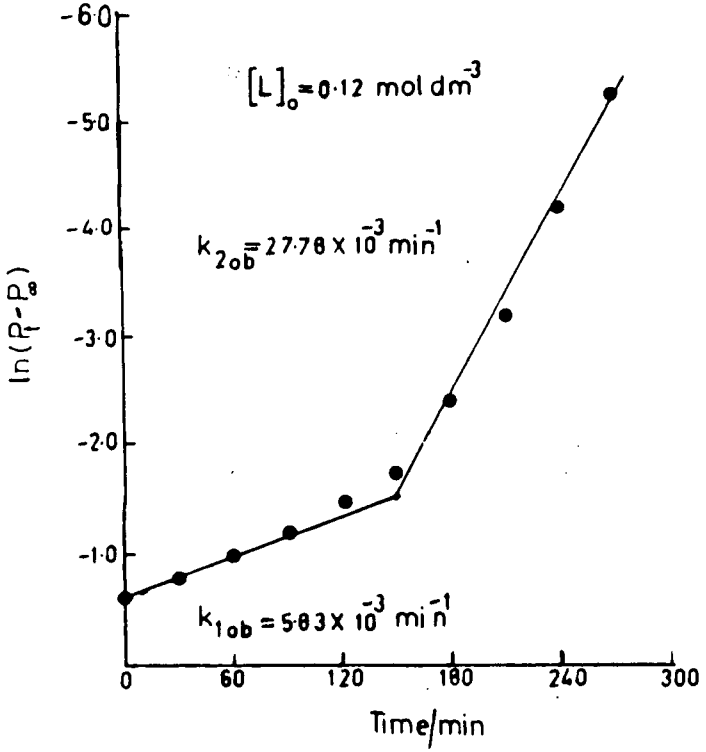


Figure 1e

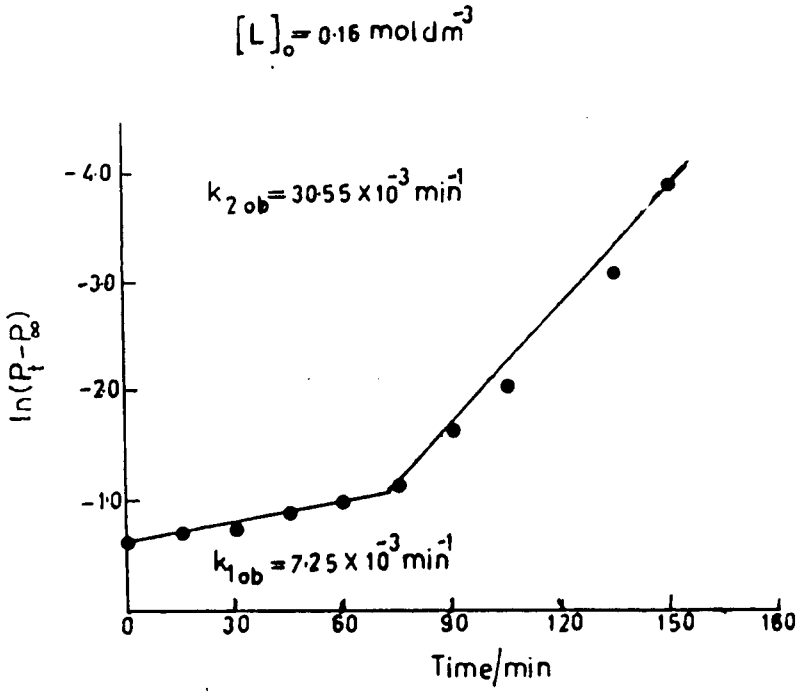


Figure 1f

Plot of $\ln(p_t - p_\infty)$ vs time in the absence of SDS

Temp = 30°C, $[H^+] = 0{\cdot}20$ mol dm^{-3}, $\mu = 0{\cdot}20$ mol dm^{-3},

$[MnO_4^-] = 2 \times 10^{-4}$ mol dm^{-3}, [SDS] = Nil

Table 3 to 5 + Figure 2a to 21

Showing effect of $[H^+]$ on the observed rate constant (k_{1ob} and k_{2ob}).

Table-3 : Effect of the $[H^+]$ on the absorbance at 530 nm in the absence of SDS.

$[H^+]$	0.20M	0.15M	0.10M	0.05M
Time	absorbance at 530 nm			
0	0.525	0.525	0.520	0.520
30	0.510	0.510	0.505	0.505
60	0.500	0.500	0.490	0.495
90	0.500	0.500	0.480	0.460
120	0.495	0.490	0.475	0.430
150	0.490	0.480	0.465	0.410
180	0.485	0.475	0.460	0.370
210	0.475	0.465	0.445	0.310
240	0.465	0.455	0.430	0.200
270	0.460	0.440	0.400	0.130
300	0.445	0.425	0.370	0.060
330	0.425	0.400	0.330	0.030
360	0.405	0.360	0.270	0.020
390	0.380	0.335	0.220	0.010
420	0.355	0.305	0.170	0.010
450	0.320	0.265	0.115	0.010
480	0.285	0.215	0.075	
510	0.250	0.175	0.055	
540	0.210	0.130	0.045	
570	0.170	0.075	0.035	
600	0.125	0.050	0.025	
630	0.085	0.030	0.020	
660	0.060	0.020	0.02	
690	0.045	0.010		
720	0.035	0.005		
750	0.025	0.005		
780	0.015			
810	0.010			

Temp. = $30^{o}C$, $[L]_o$ = 0.02 mol dm^{-3}, μ = 0.20 mol dm^{-3}, $[MnO_4^-]$ = 2×10^{-4}, mol dm^{-3}, [SDS] = Nil.

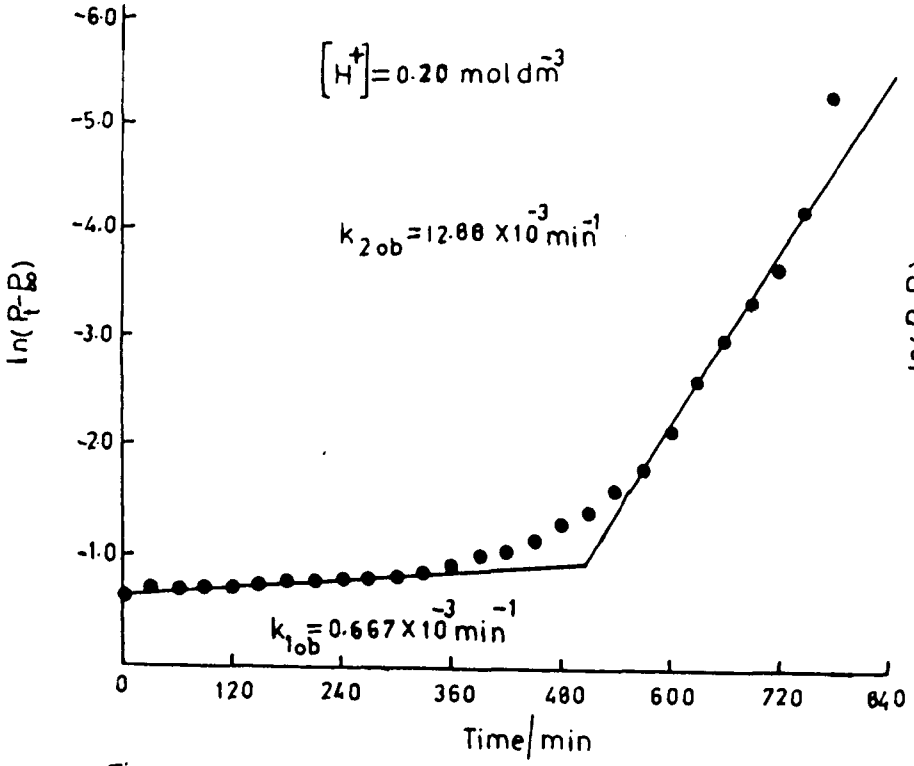


Figure 2a

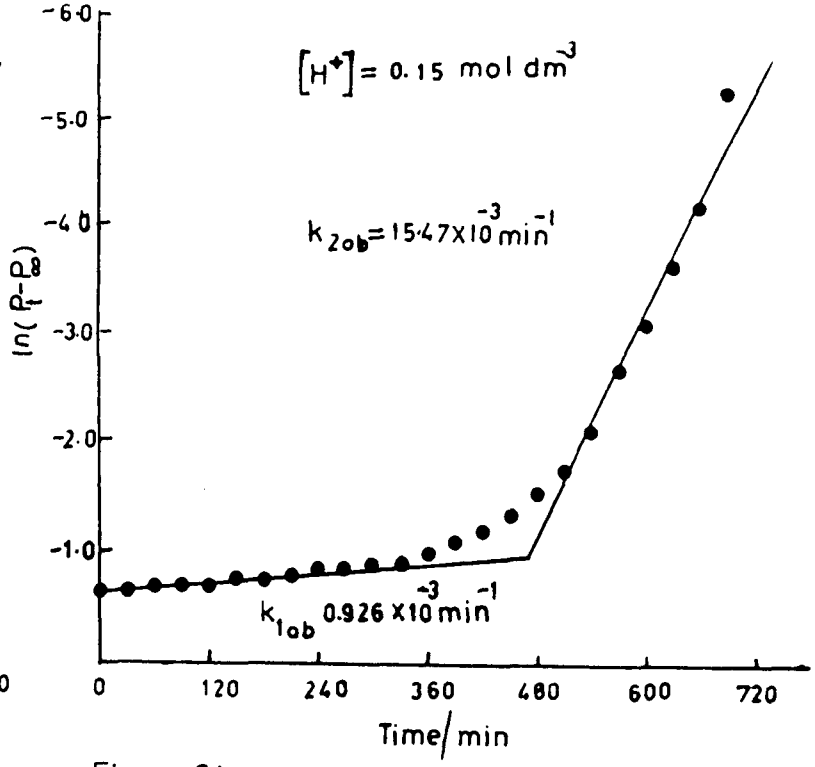


Figure 2b

Plot of $\ln(P_t - P_\infty)$ VS time in the absence of SDS
Temp=30°C, $[L]_o$=0.02 mol dm^{-3}, μ=0.20 mol dm^{-3},
$[MnO_4^-]$ = 2X10^{-4} mol dm^{-3}, [SDS]=Nil

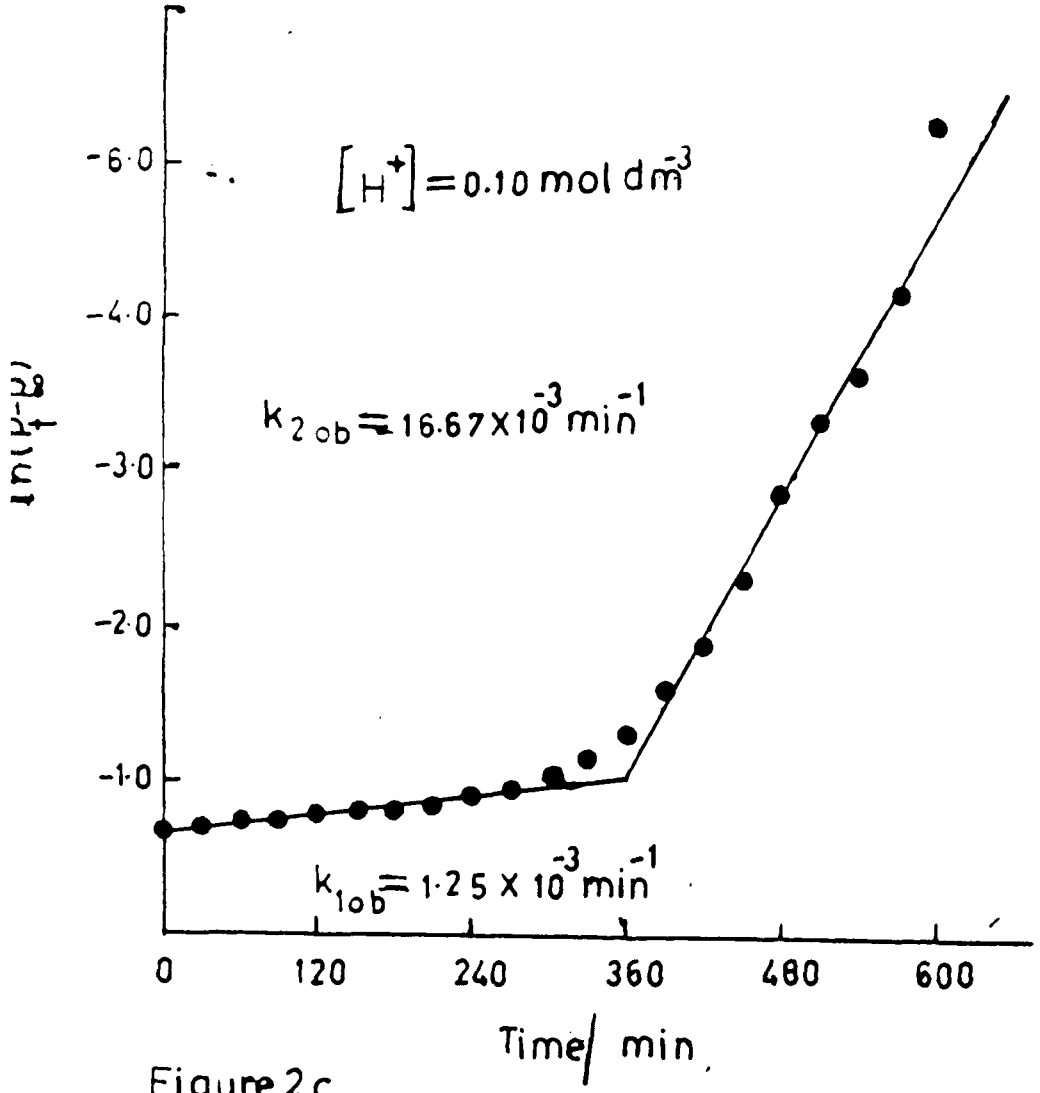


Figure 2c

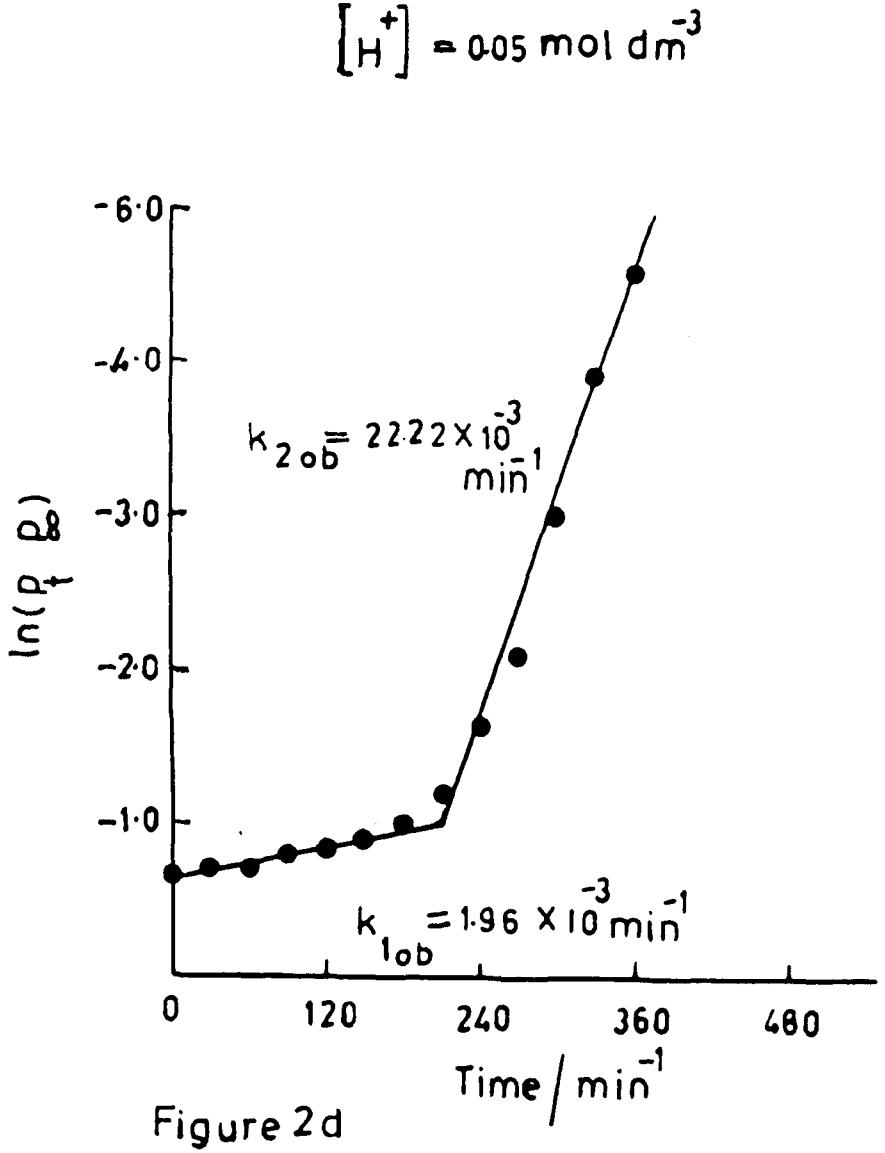


Figure 2d

Plot of $\ln(P_t - P_\infty)$ VS time in the absence of SDS

Temp = 30°C, $[L]_o = 0.02$ mol dm^{-3}, $\mu = 0.20$ mol dm^{-3},

$[MnO_4^-] = 2 \times 10^{-4}$ mol dm^{-3}, [SDS] = Nil

Table-4 : Effect of the $[H^+]$ on the absorbance at 530 nm in the absence of SDS.

$[H^+]$	0.20M	0.15M	0.10M	0.05M
Time	absorbance at 530 nm			
0	0.530	0.530	0.530	0.530
30	0.520	0.520	0.515	0.500
60	0.510	0.505	0.480	0.420
90	0.500	0.480	0.450	0.360
120	0.480	0.460	0.420	0.320
150	0.470	0.440	0.380	0.260
180	0.450	0.410	0.340	0.190
210	0.430	0.385	0.300	0.140
240	0.395	0.350	0.260	0.100
270	0.380	0.320	0.220	0.075
300	0.330	0.280	0.175	0.050
330	0.290	0.230	0.135	0.040
360	0.265	0.200	0.115	0.030
390	0.230	0.160	0.100	0.020
420	0.200	0.145	0.080	0.015
450	0.170	0.122	0.060	0.010
480	0.135	0.085	0.050	0.010
510	0.110	0.060	0.040	0.010
540	0.085	0.035	0.030	
570	0.065	0.020	0.020	
600	0.040	0.015	0.010	
630	0.035	0.010	0.010	
660	0.025	0.010	0.010	
690	0.015	0.010		
720	0.010			
750	0.010			

Temp. = 30°C, $[L]_o$ = 0.04 mol dm^{-3}, μ = 0.20 mol dm^{-3}

$[MnO_4^-]$ = 2×10^{-4} mol dm^{-3}, [SDS] = Nil

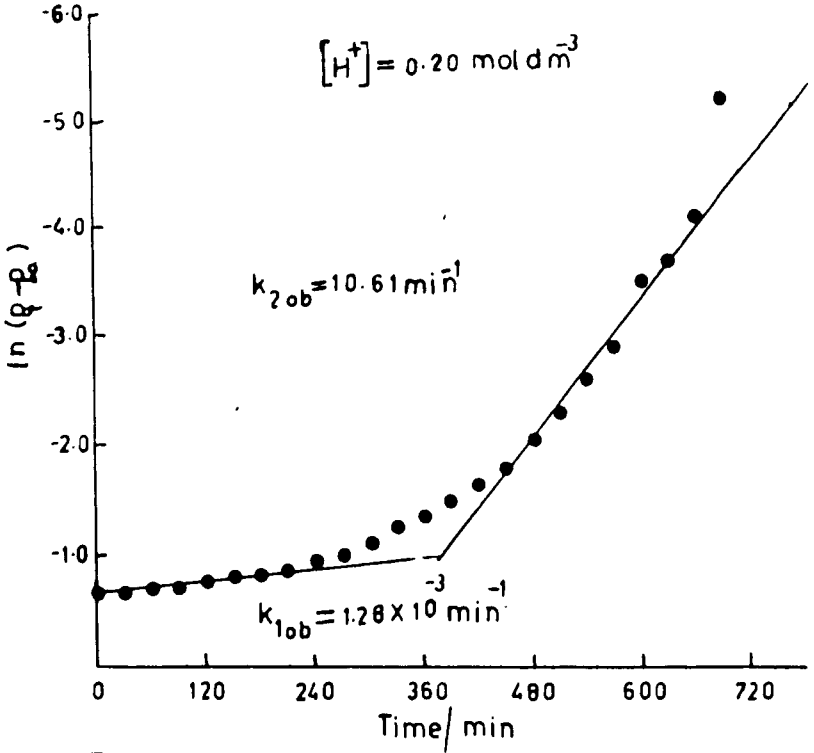


Figure 2e

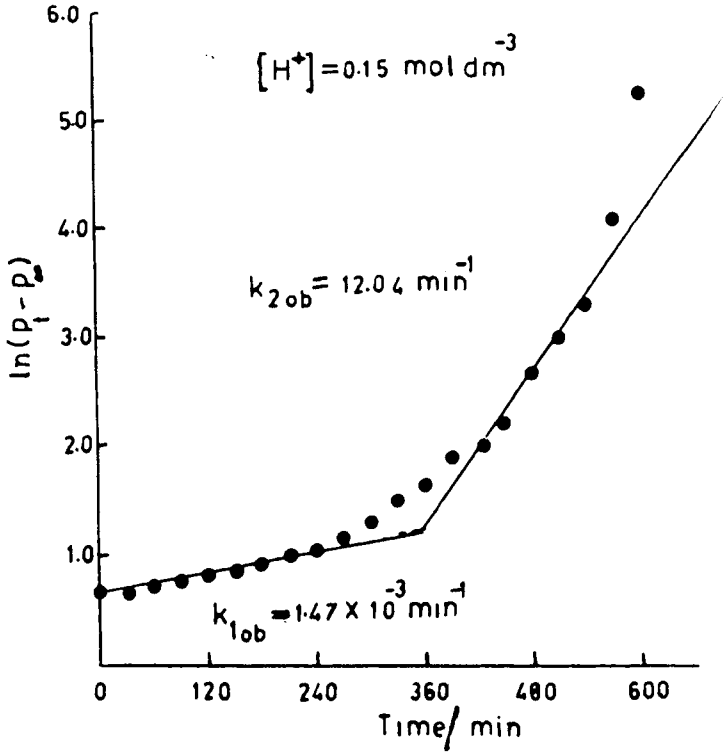


Figure 2f

Plot of $\ln(P_t - P_\infty)$ VS time in the absence of SDS
Temp = 30°C, $[L]_o$ = 0.04 mol dm^{-3}, μ = 0.20 mol dm^{-3},
$[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS] = Nil

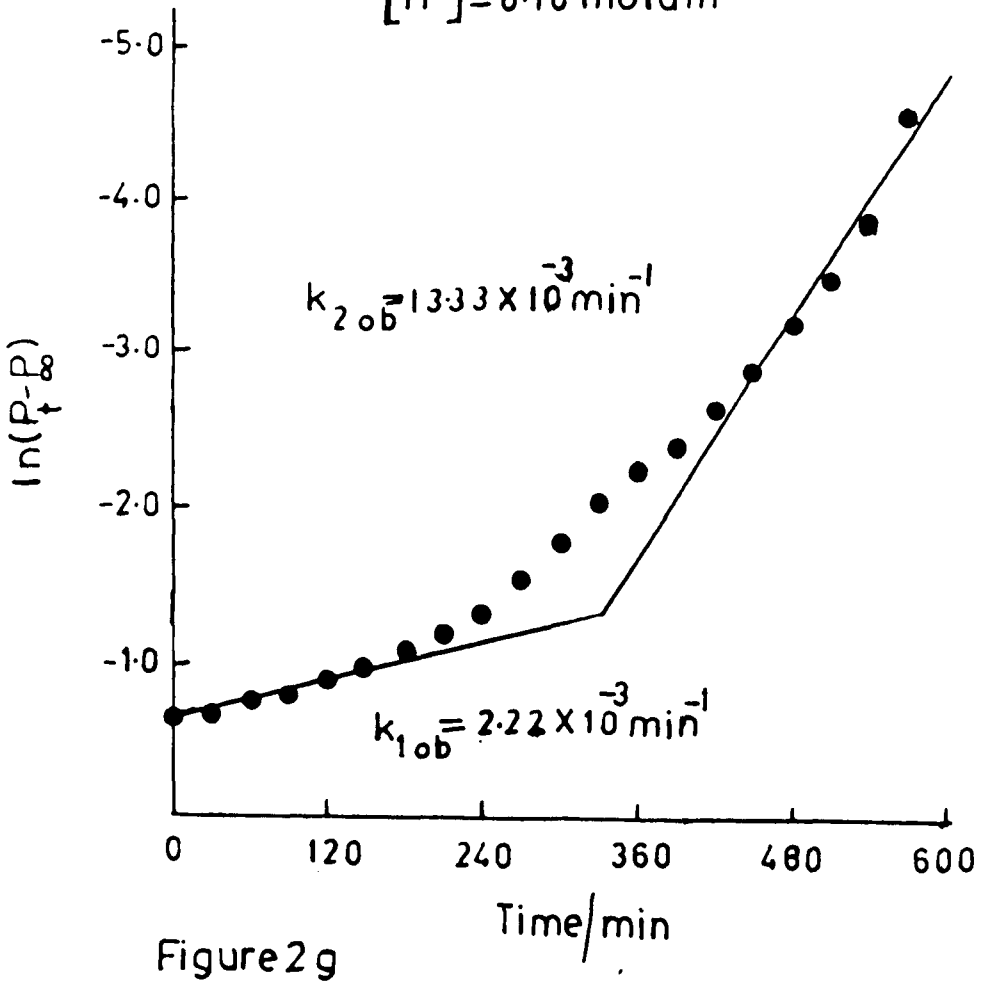


Figure 2g

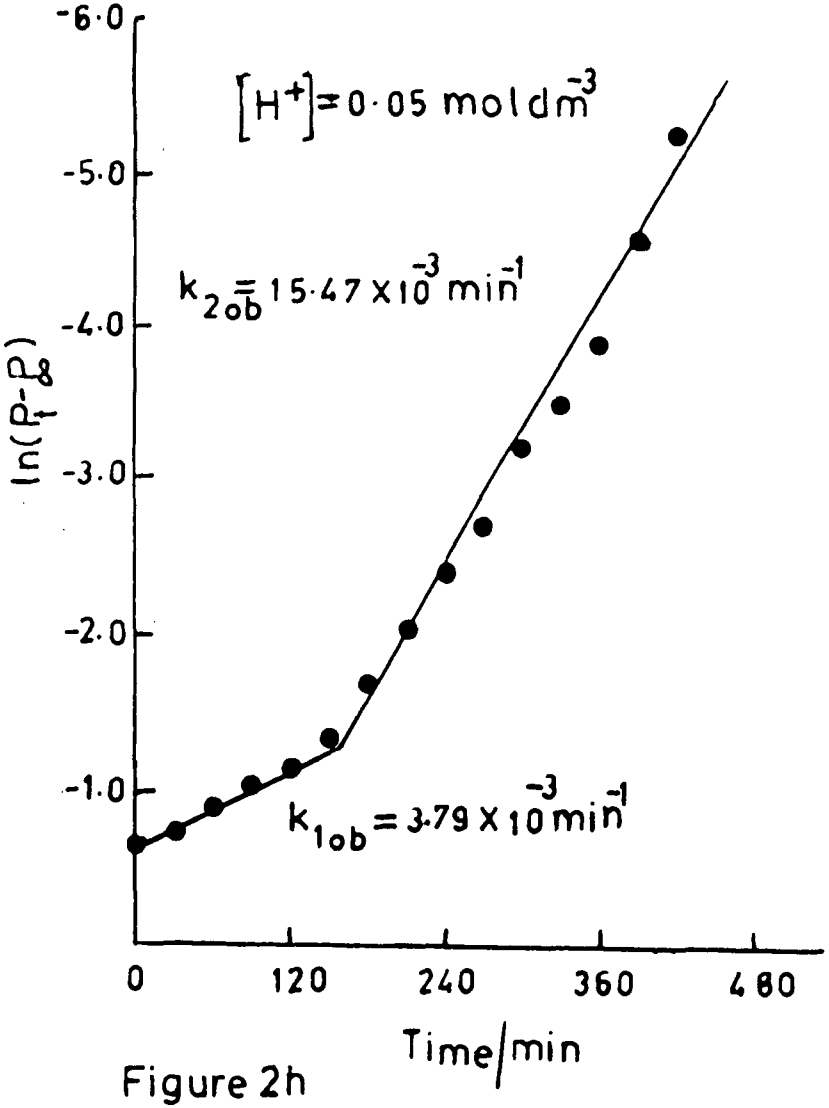


Figure 2h

Plot of $\ln(P_t - P_\infty)$ VS time in absence of SDS

Temp = 30°C, $[L]_o$ = 0·04 mol dm^{-3}, μ = 0·20 mol dm^{-3},

$[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS] = Nil

Table-5: Effect of the $[H^+]$ on the absorbance at 530 nm in the absence of SDS.

$[H^+]$	0.20M	0.15M	0.10M	0.05M
Time	absorbance at 530 nm			
0	0.525	0.520	0.520	0.520
15	0.510	0.500	0.500	0.500
30	0.495	0.490	-	-
45	0.485	0.480	0.460	0.440
60	0.470	0.460	-	-
75	0.460	0.450	0.400	0.370
90	0.440	0.425	-	-
105	0.430	0.405	0.320	0.280
120	0.410	0.375	-	-
135	0.390	0.350	0.250	0.200
150	0.375	0.325	-	-
165	0.355	0.300	0.185	0.130
180	0.340	-	-	-
195	0.320	0.250	0.130	0.070
210	0.305	-	-	-
225	0.285	0.200	0.080	0.030
240	0.260	-	-	-
255	0.245	0.155	0.045	0.015
270	0.225	-	-	-
285	0.205	0.115	0.020	0.005
300	0.185	-	-	-
315	0.170	0.085	0.010	0.005
330	0.150	-	-	
345	0.130	0.050	0.010	
360	0.115	-		
375	0.090	0.030		
405	0.060	0.020		
420	0.040	-		
435	-	0.010		
450	0.030	0.010		
480	0.020			
540	0.010			

Temp. = 30°C, $[L]_o$ = 0.08 mol dm^{-3}, μ = 0.20 mol dm^{-3}
$[MnO_4^-]$ = 2×10^{-4} mol dm^{-3}, [SDS] = Nil.

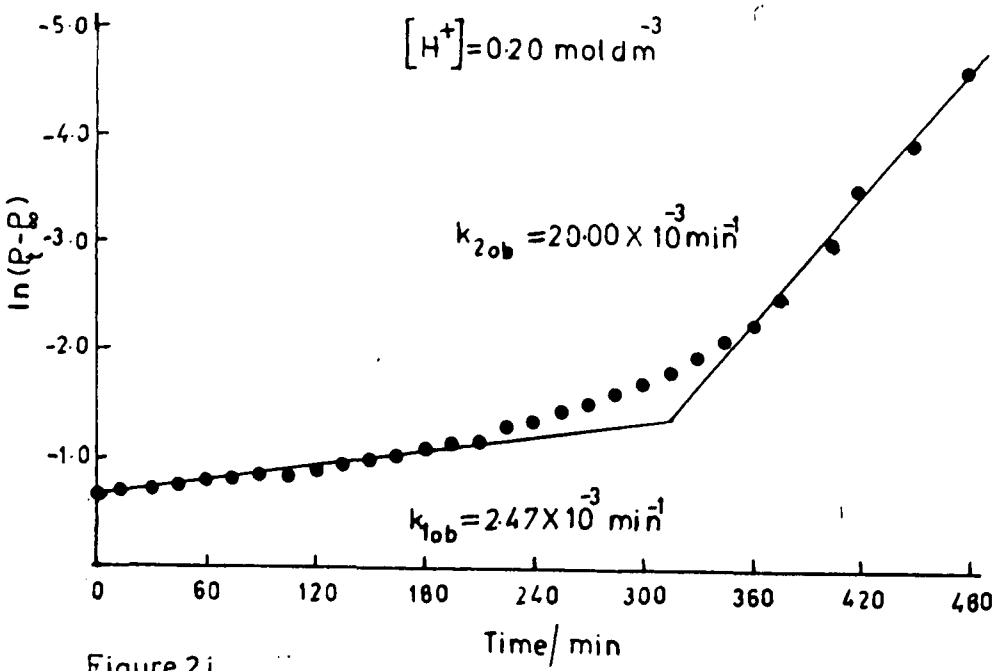


Figure 2 i

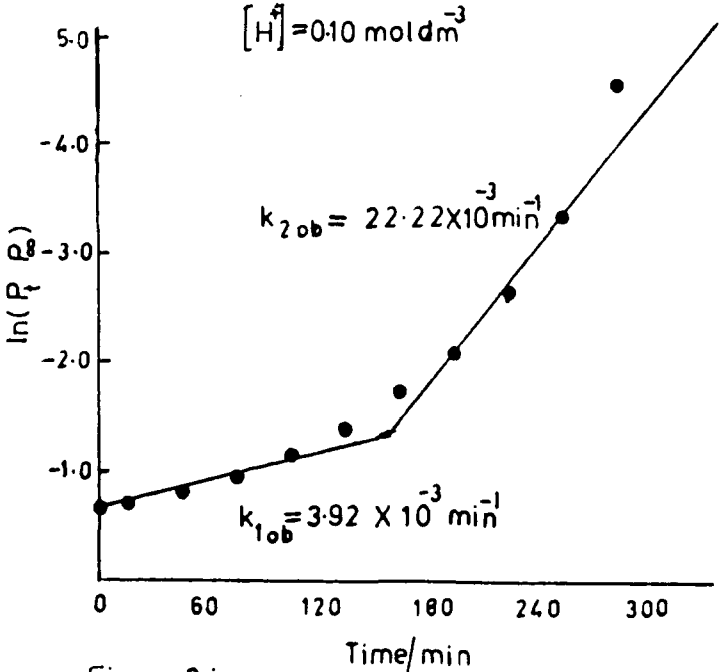


Figure 2 j

Plot of $\ln(P_t - P_\infty)$ VS time in the absence of SDS

Temp = 30°C, $[L]_o$ = 0·08 mol dm^{-3}, μ = 0·20 mol dm^{-3},

$[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS] = Nil

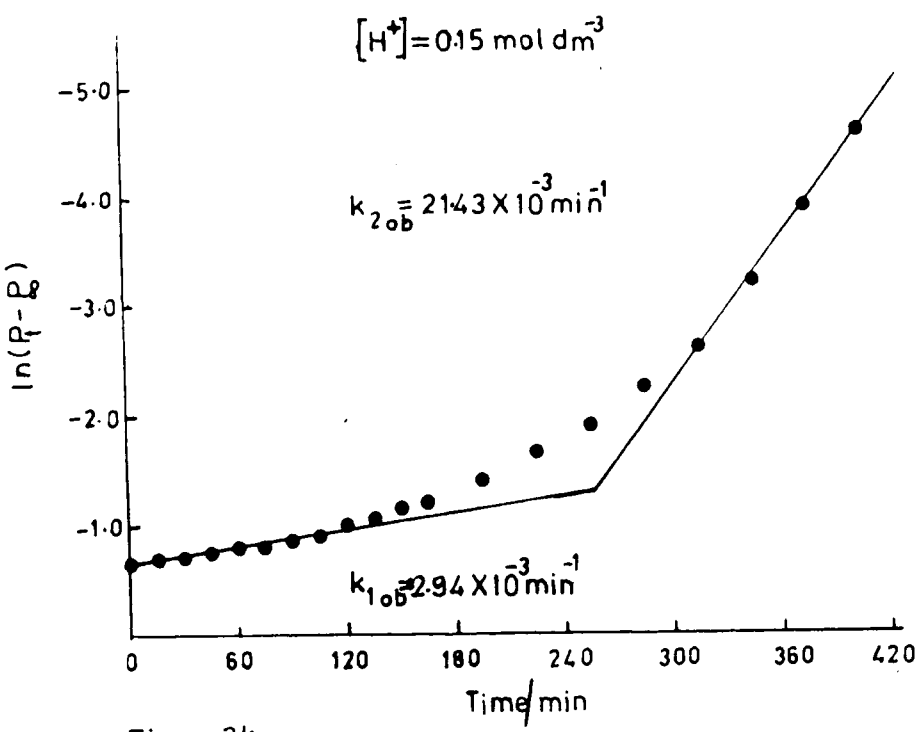


Figure 2k

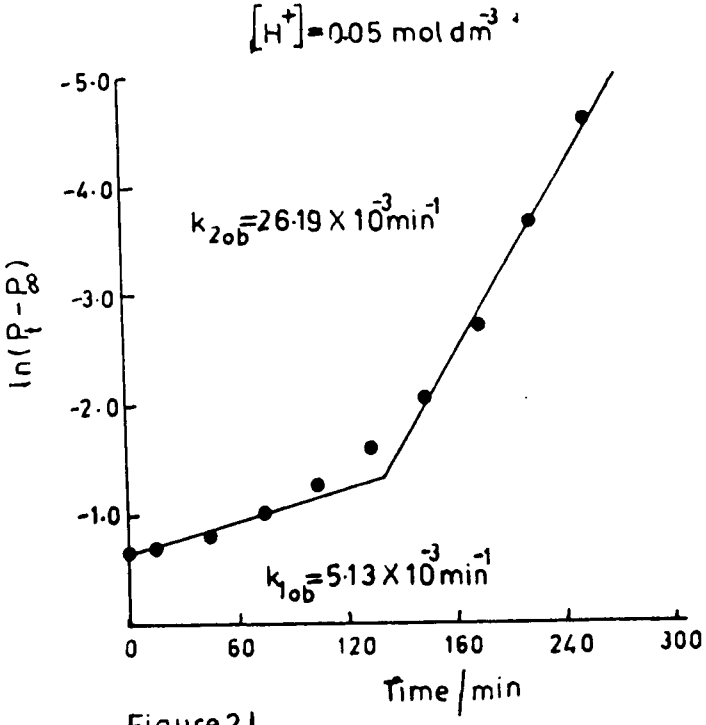


Figure 2l

Plot of $\ln(P_t - P_\infty)$ VS time in the absence of SDS

Temp = 30°C, $[L]_o$ = 0·08 mol dm^{-3}, μ = 0·20 mol dm^{-3}

$[MnO_4^-]$ = 2 X 10 mol dm^{-3}, [SDS] = Nil

Table 6 to 8 + Figure 3a to 3i

Showing effect of temperature on the rate constant (k_{1ob} and k_{2ob}).

Table-6 : Effect of temperature on absorbance at 530 nm in the absence of SDS.

Lysine	0.02M	0.04M	0.08M
Time	absorbance at 530 nm		
0	0.520	0.520	0.510
30	0.515	0.510	0.500
60	0.510	0.500	0.480
90	0.500	0.490	0.460
120	0.490	0.480	0.435
150	0.485	0.470	0.415
180	0.480	0.455	0.380
210	0.475	0.435	0.360
240	0.465	0.425	0.330
270	0.455	0.415	0.300
300	0.445	0.395	0.270
330	0.440	0.385	0.245
360	0.435	0.375	0.225
390	0.430	0.335	0.200
420	0.420	0.300	0.180
450	0.410	0.275	0.160
480	0.400	0.250	0.140
510	0.385	0.220	0.110
540	0.340	0.200	0.080
570	0.300	0.170	0.065
600	0.280	0.140	0.050
630	0.255	0.115	0.045
660	0.210	0.090	0.040
690	0.170	0.060	0.035
720	0.140	0.040	0.030
750	-	0.030	0.030
780	0.100	0.025	-
810	-	0.020	
840	0.075	0.015	
870	-	0.010	
900	0.040	0.010	

Temp. = 30°C, $[H^+]$ = 0.20 mol dm^{-3}, μ = 0.20 mol dm^{-3}, $[MnO_4^-]$ = 2×10^{-4} mol dm^{-3}, [SDS] = Nil

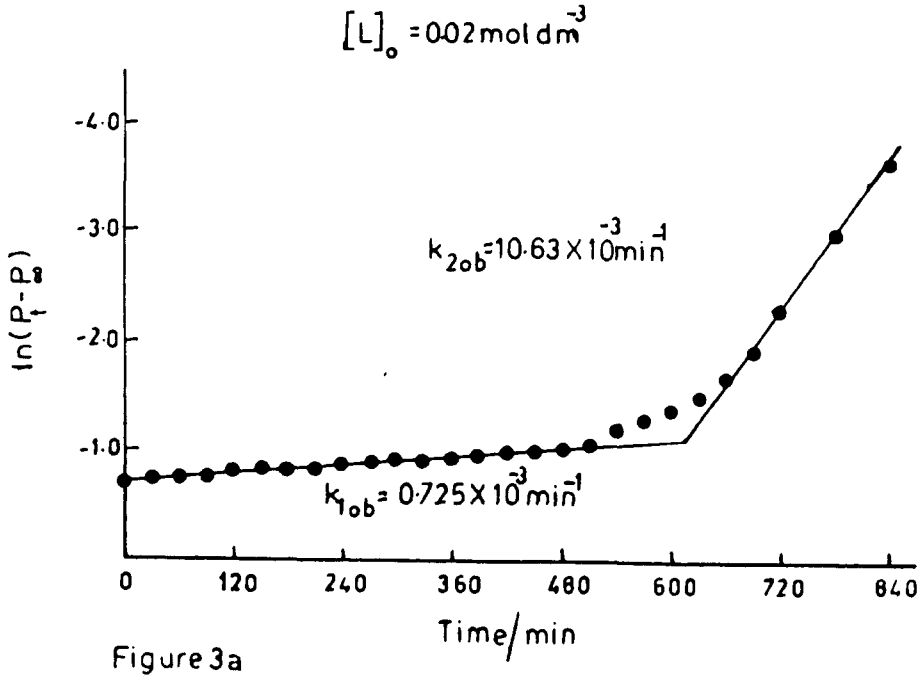


Figure 3a

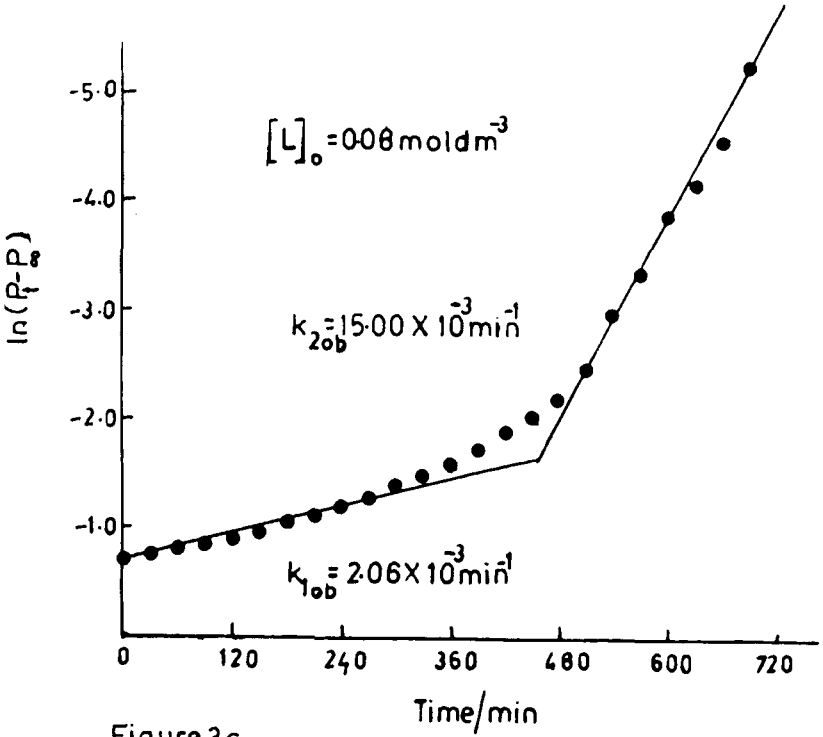


Figure 3c

Plot of $\ln(P_t - P_\infty)$ VS time in the absence of SDS

Temp = 30°C, $[H^+] = 0.20 mol dm^{-3}$, $\mu = 0.20 mol dm^{-3}$,

$[MnO_4^-] = 2 \times 10^{-4} mol dm^{-3}$, [SDS] = Nil

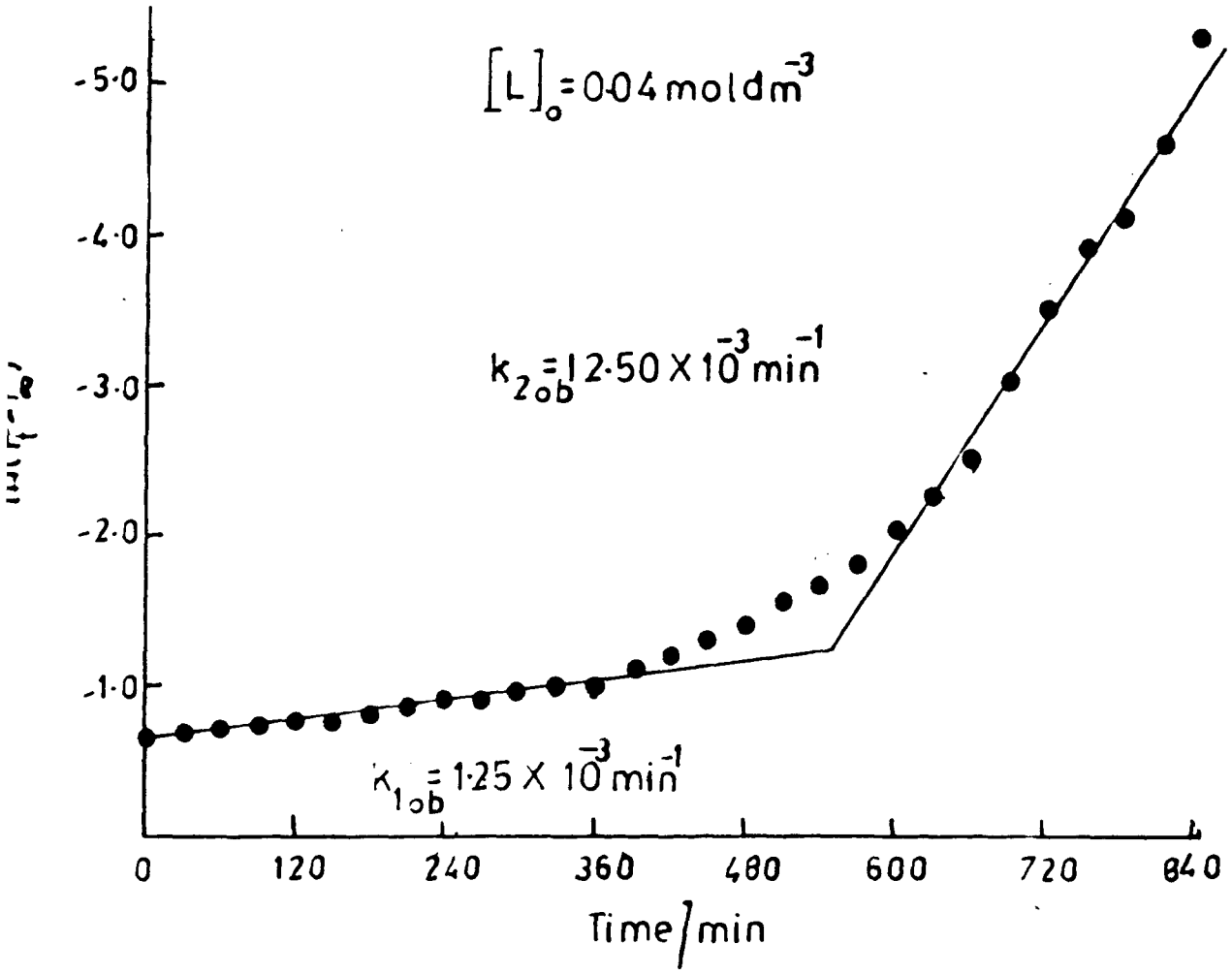


Figure 3b Plot of $\ln(P_t - P_\infty)$ VS time in the absence of SDS
Temp = 30°C, $[H^+]$ = 0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3},
$[MnO_4^-]$ = 2 X 10^{-3} mol dm, [SDS] = Nil

Table-7 : Effect of temperature on absorbance at 530 nm in the absence of SDS.

Lysine	0.02M	0.04M	0.08M
Time	absorbance at 530 nm		
0	0.525	0.525	0.525
30	0.520	0.510	-
45	-	-	0.485
60	0.500	0.495	-
75	-	-	0.460
90	0.500	0.490	-
105	-	-	0.430
120	0.495	0.480	-
135	-	-	0.390
150	0.490	0.470	-
165	-	-	0.355
180	0.485	0.455	-
195	-	-	0.320
210	0.475	0.430	-
225	-	-	0.285
240	0.465	0.395	-
255	-	-	0.240
270	0.460	0.365	-
285	-	-	0.205
300	0.445	0.330	-
315	-	-	0.170
330	0.425	0.290	-
345	-	-	0.130
360	0.405	0.265	-
375	-	-	0.090
390	0.380	0.230	-
405	-	-	0.060
420	0.355	0.200	-
435	-	-	0.030
450	0.320	0.170	-
465	-	-	0.020
480	0.285	0.135	0.020
510	0.250	0.110	
540	0.210	0.085	
570	0.170	0.065	
600	0.125	0.040	
630	0.085	0.025	
660	0.050	0.015	
690	0.035	0.010	
720	0.025	0.010	
750	0.015		
780	0.010		
810	0.010		

Temp. = 35°C, $[H^+]$ = 0.20 mol dm^{-3}, μ = 0.20 mol dm^{-3}
$[MnO_4^-]$ = 2×10^{-4} mol dm^{-3}, [SDS] = Nil.

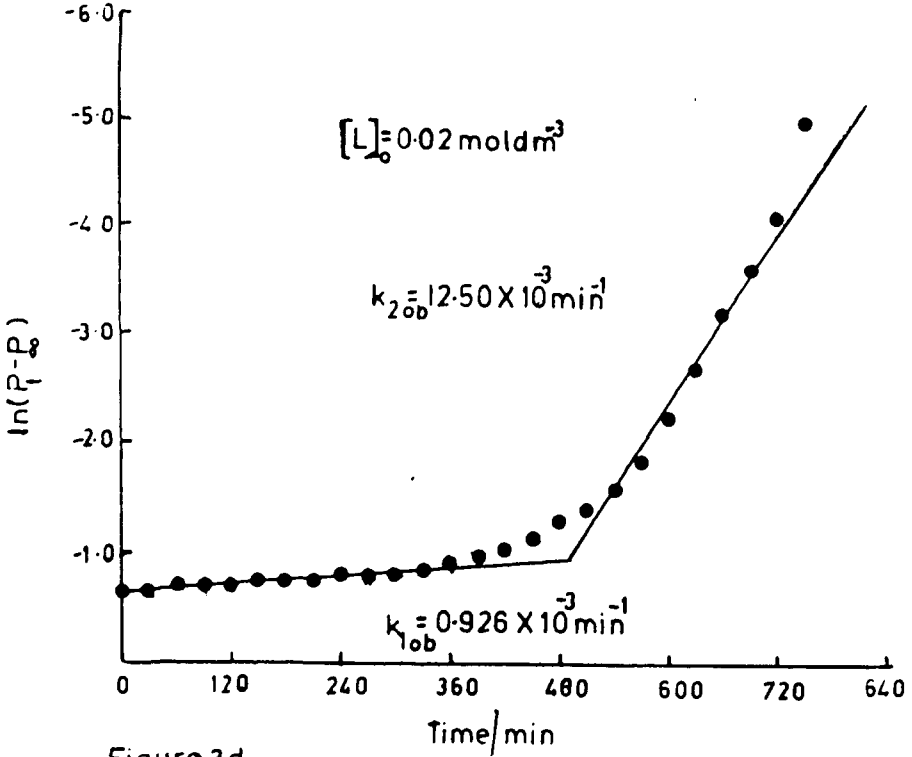


Figure 3d

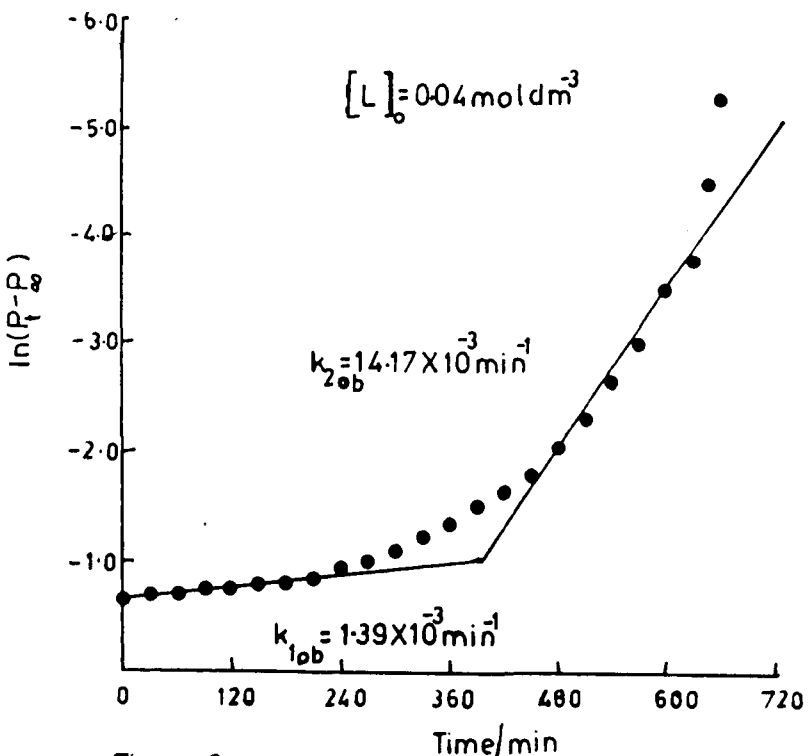


Figure 3e

Plot of $\ln(P_t - P_\infty)$ VS time in the absence of SDS

Temp = 35°C, $[H^+] = 0{\cdot}20\ mol\,dm^{-3}$, $\mu = 0{\cdot}20\ mol\,dm^{-3}$,

$[MnO_4^-] = 2 \times 10^{-4}\ mol\,dm^{-3}$, $[SDS]$ = Nil

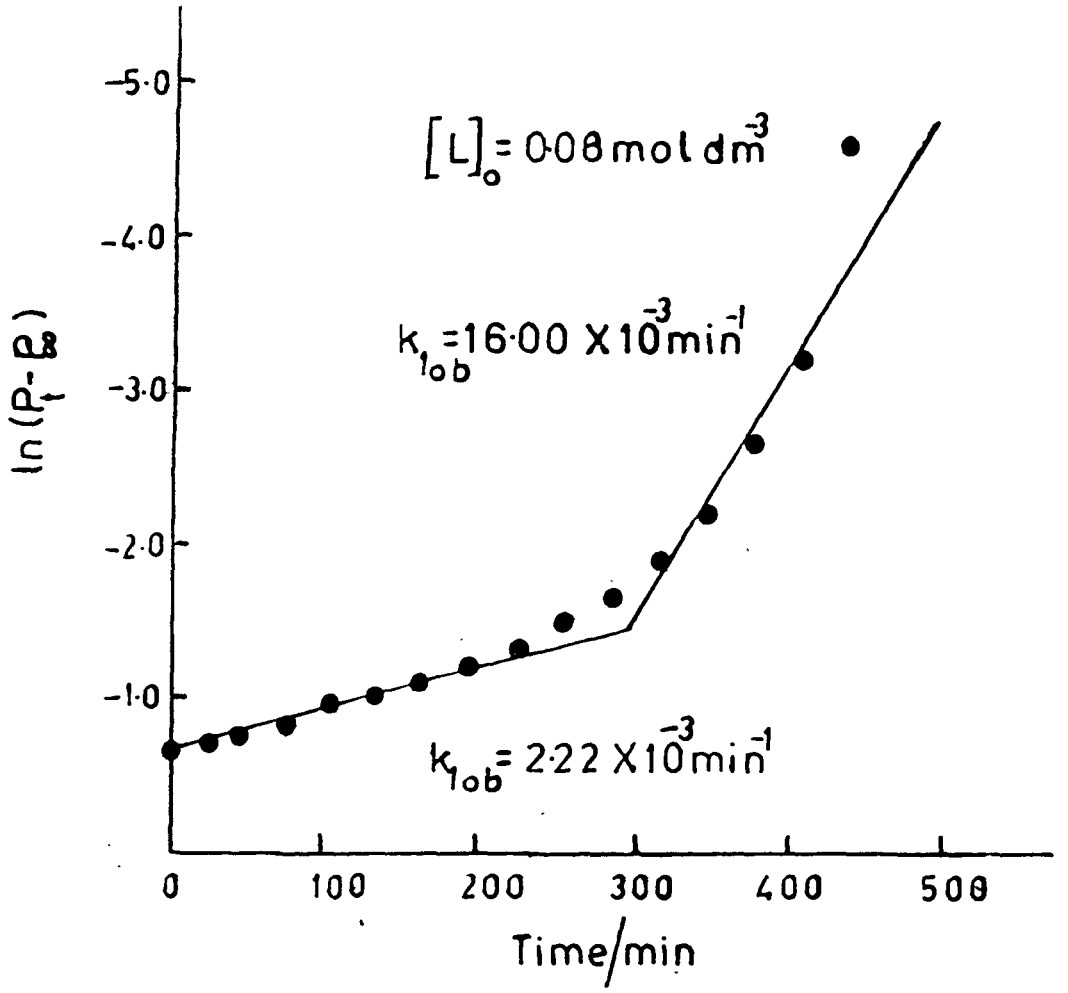


Figure 3f Plot of $\ln(P_t - P_\infty)$ VS time in the absence of SDS

Temp = 35°C, $[H^+] = 0{\cdot}20$ mol dm^{-3}, $\mu = 0{\cdot}20$ mol dm^{-3},

$[MnO_4^-] = 2 \times 10^{-4}$ mol dm^{-3}, [SDS] = Nil

Table-8 : Effect of temperature on absorbance at 530 nm in the absence of SDS.

Lysine	0.02M	0.04M	0.08M
Time	absorbance at 530 nm		
0	0.525	0.525	0.525
30	0.520	0.510	0.500
60	0.510	0.510	0.475
90	0.510	0.490	0.440
120	0.500	0.480	0.385
150	0.490	0.460	0.330
180	0.480	0.435	0.280
210	0.465	0.405	0.220
240	0.450	0.370	0.170
270	0.420	0.320	0.120
300	0.390	0.270	0.085
330	0.350	0.215	0.060
360	0.310	0.160	0.040
390	0.260	0.110	0.025
420	0.220	0.080	0.015
450	0.160	0.055	0.010
480	0.125	0.035	0.010
510	0.100	0.020	
540	0.090	0.010	
600	0.080	0.010	
630	0.080		

Temp. = $40^{o}C$, $[H^{+}] = 0.20$ mol dm^{-3}, $\mu = 0.20$ mol dm^{-3}

$[MnO_4^{-}] = 2 \times 10^{-4}$ mol dm^{-3}, [SDS] = Nil

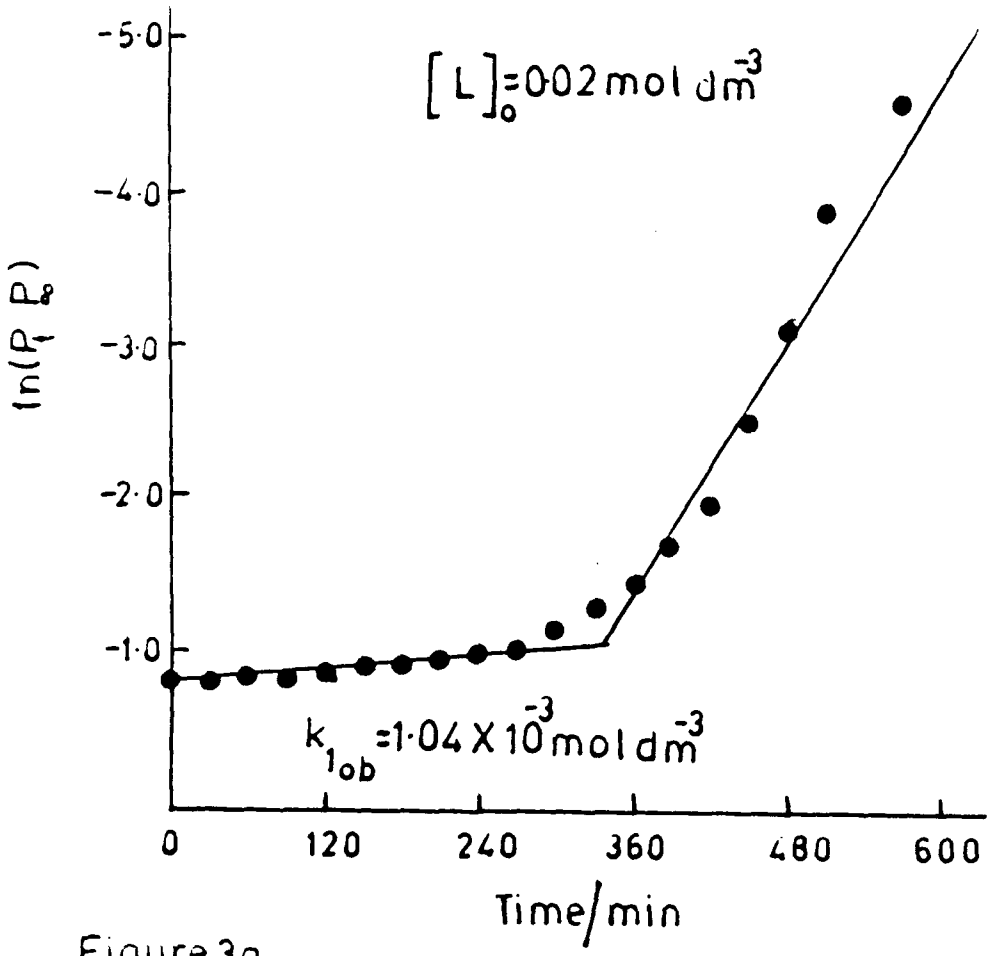


Figure 3g

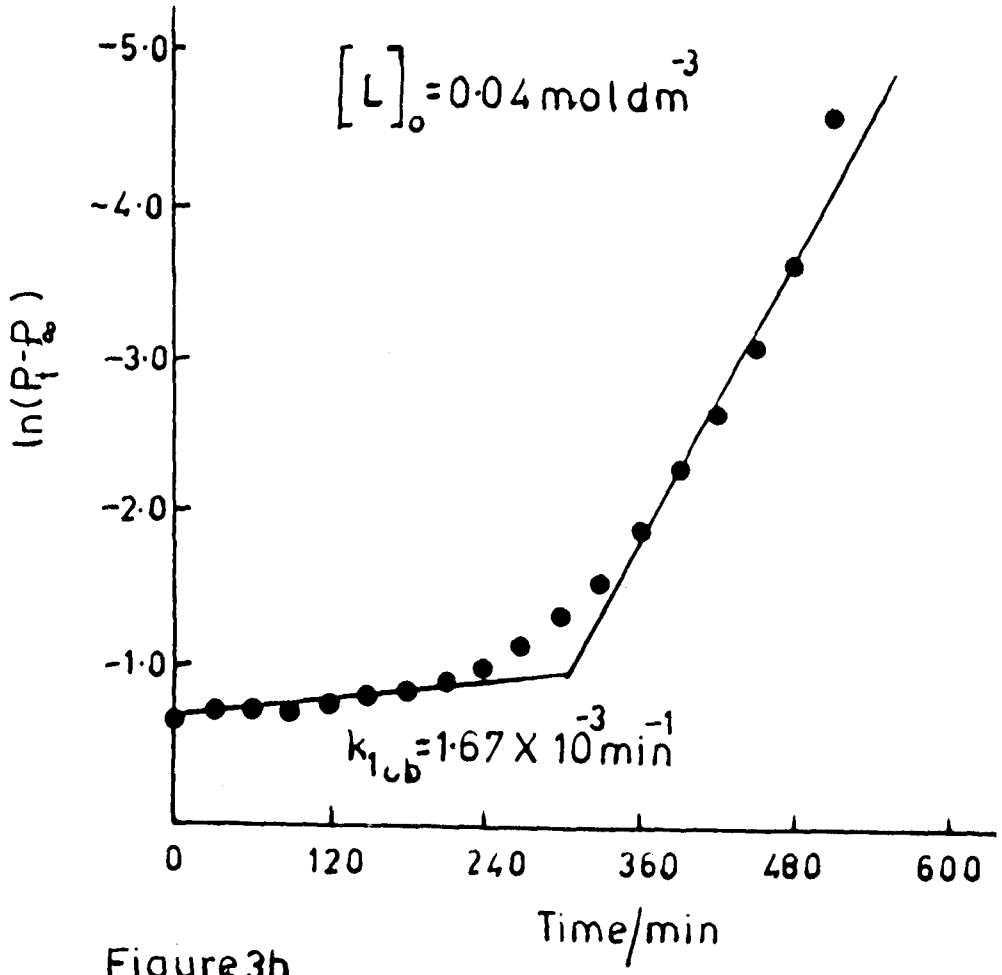


Figure 3h

Plot of $\ln(P_t - P_\infty)$ VS time in the absence of SDS

Temp=40°C, $[H^+]$ 0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3},

$[MnO_4^-]$=2 X 10^{-3} mol dm^{-3}; [SDS]=Nil

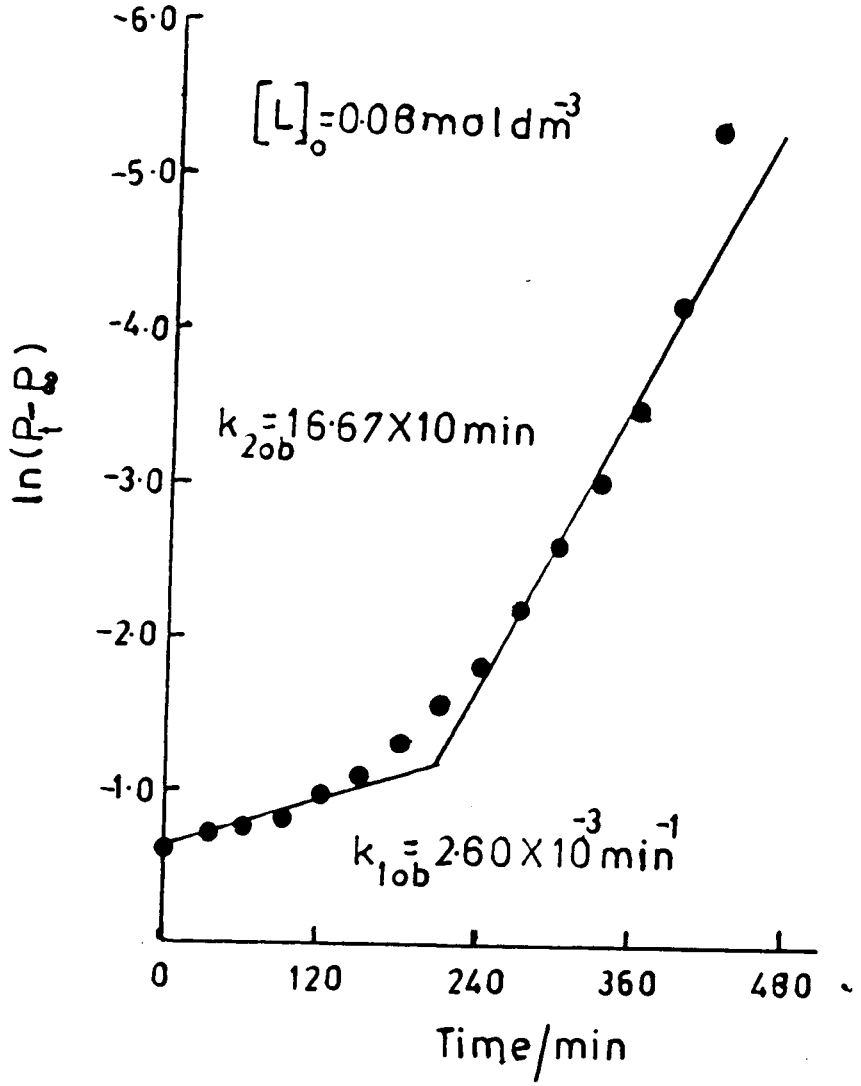


Figure 3i Plot of $\ln(P_t - P_\infty)$ VS time in the absence of SDS

Temp = 40°C, $[H^+] = 0{\cdot}20 mol dm^{-3}$, $\mu = 0{\cdot}20 mol dm^{-3}$,

$[MnO_4^-] = 2 X 10^{-4} mol dm^{-3}$, $[SDS]$ = Nil

OXIDATION OF LYSINE IN THE PRESENCE OF SDS :

Table 9 + Figure 4a to 4e

Showing effect of the concentration of lysine on the observed rate constant (k^{s}_{1ob} and k^{s}_{2ob}).

Table-9 : Effect of the concentration of lysine on the absorbance at 530 nm in the presence of SDS.

Lysine	0.02M	0.04M	0.10M	0.12M	0.16M
Time	absorbance at 530 nm				
0	0.510	0.510	0.510	0.510	0.510
15	0.460	0.440	0.400	0.400	0.375
30	0.425	0.415	-	-	-
45	0.400	0.375	0.250	-	0.150
60	0.360	0.340	0.190	0.160	0.065
75	0.320	0.295	0.140	0.095	0.020
90	0.280	0.260	0.090	0.060	0.010
105	0.230	0.215	-	0.045	-
120	0.175	0.180	0.040	0.025	0.005
135	0.111	0.150	-	-	0.005
150	0.100	0.115	0.020	0.010	
165	0.070	0.090	-		
180	0.050	0.065	-		
195	0.040	0.040	0.010		
210	0.030	0.030			
225	0.025	0.020	0.010		
240	0.020	0.015			
255	0.015	0.010			
270	0.015	0.010			

Temp. = 30°C, $[H^+]$ = 0.20 mol dm^{-3}, μ = 0.20 mol dm^{-3}, $[MnO_4^-]$ = 2×10^{-4} mol dm^{-3}, [SDS] = 0.01 mol dm^{-3}.

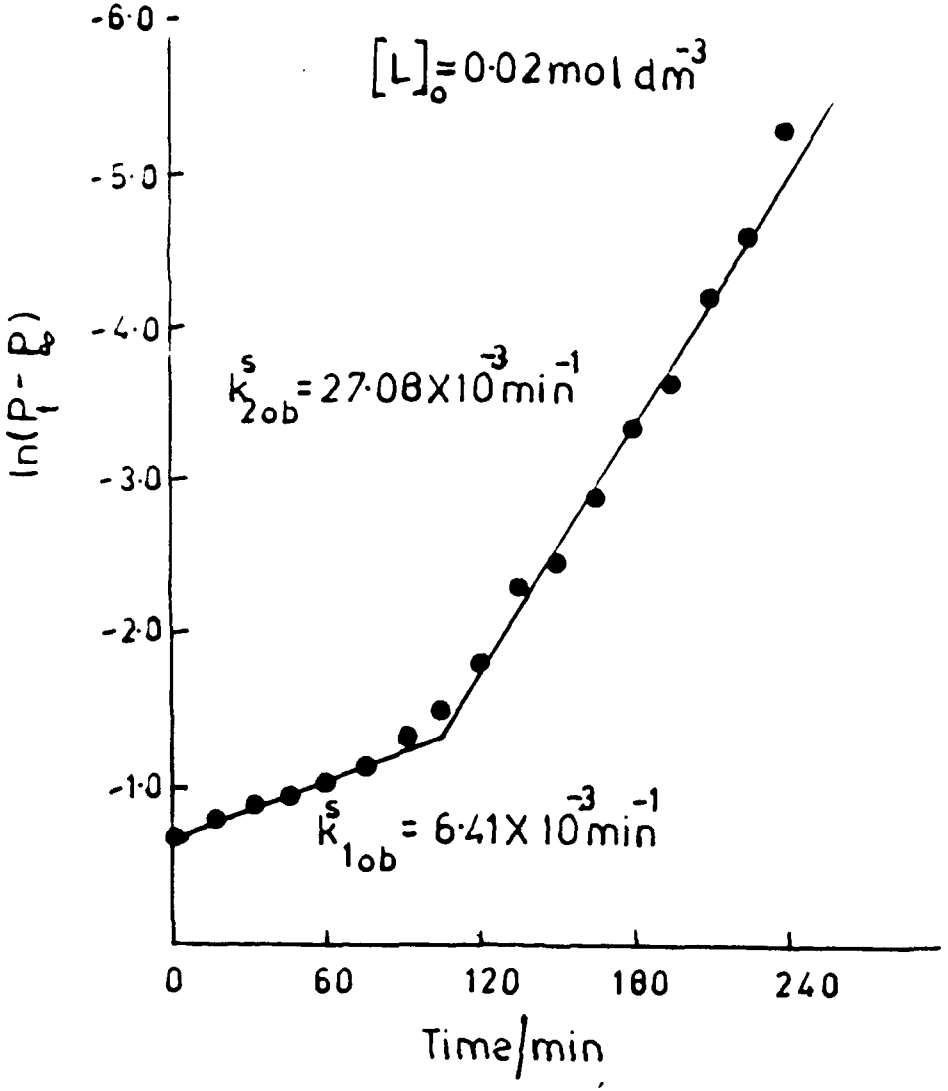


Figure 4a

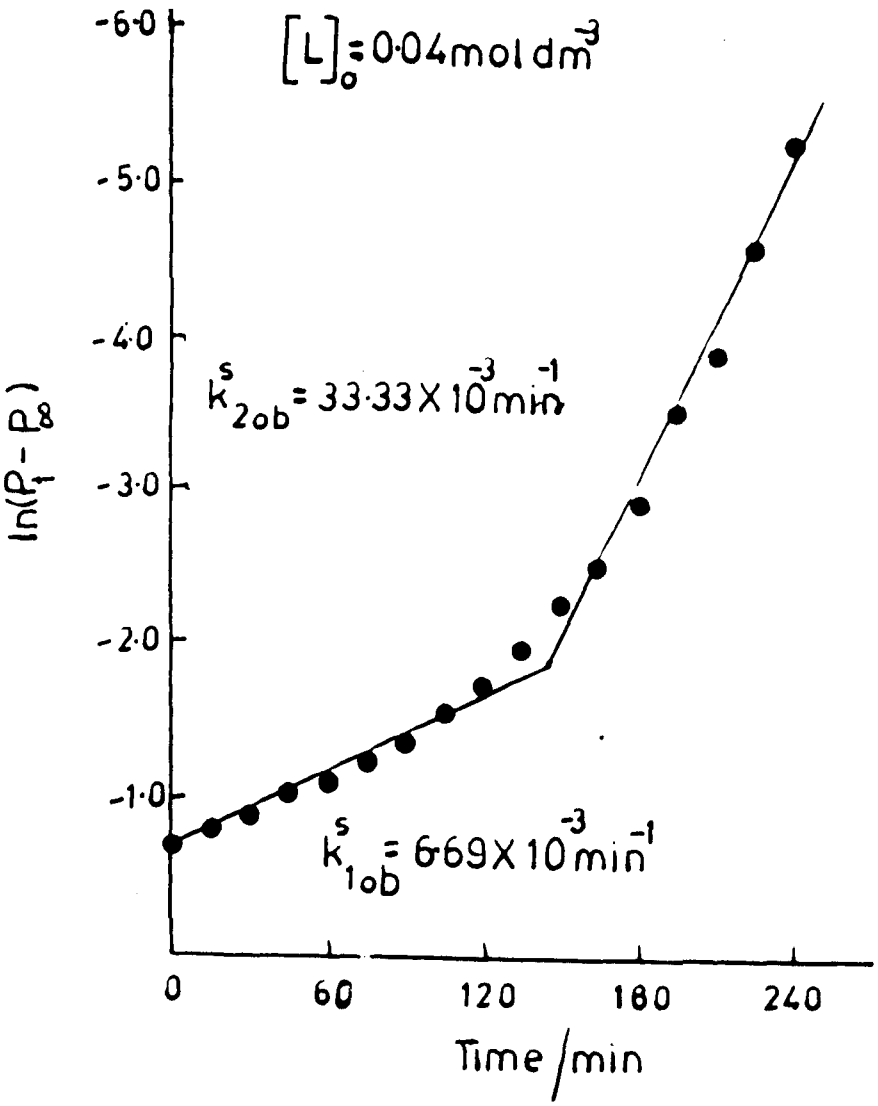


Figure 4b

Plot of $\ln(P_t - P_\infty)$ VS time in the presence of SDS

Temp = 30°C, $[H^+] = 0{\cdot}20$ mol dm^{-3}, $\mu = 0{\cdot}20$ mol dm^{-3},

$[MnO_4^-] = 2 \times 10^{-4}$ mol dm^{-3}, $[SDS] = 0{\cdot}01$ mol dm^{-3}

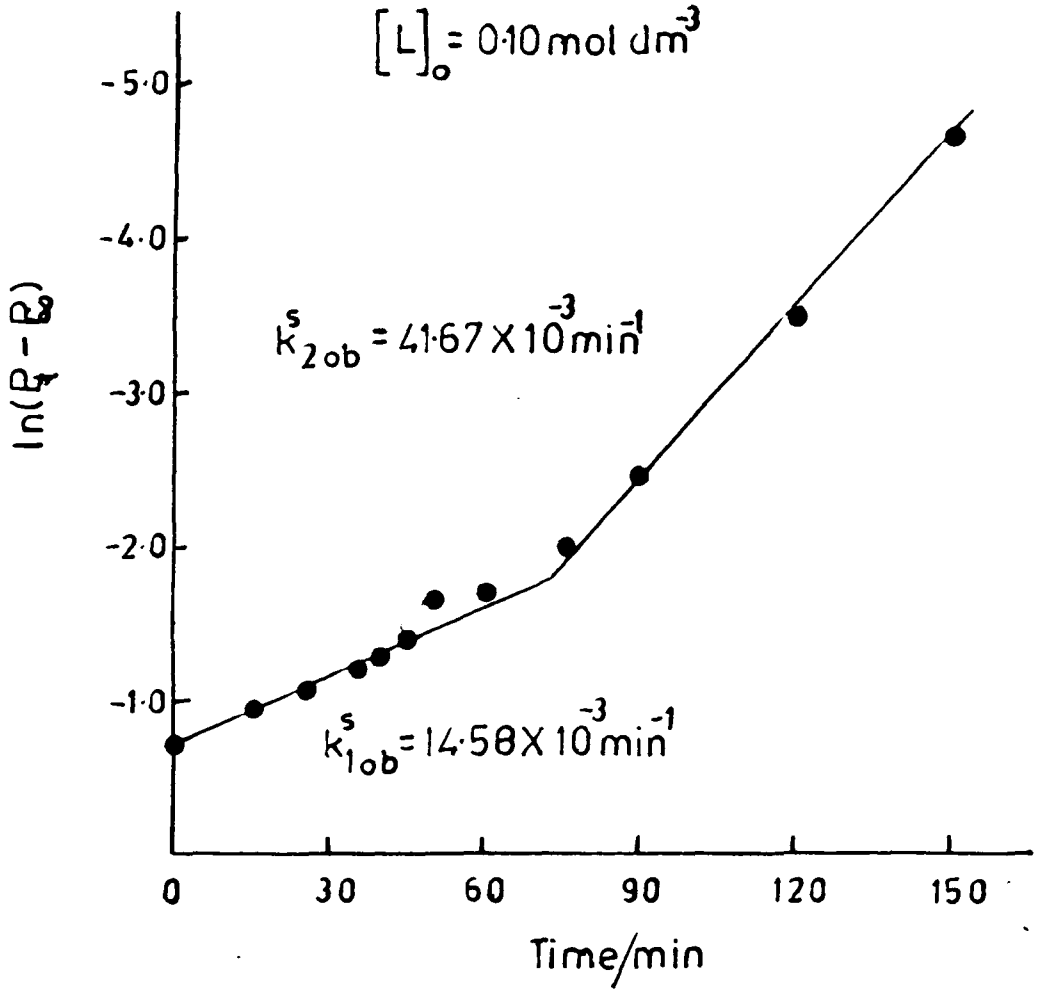


Figure 4c Plot of $\ln(P_t - P_\infty)$ VS time in the presence of SDS
Temp = 30°C, $[H^+] = 0{\cdot}20\,mol\,dm^{-3}$, $\mu = 0{\cdot}20\,mol\,dm^{-3}$,
$[MnO_4^-] = 2 \times 10^{-4}\,mol\,dm$, $[SDS] = 0{\cdot}10\,mol\,dm^{-3}$

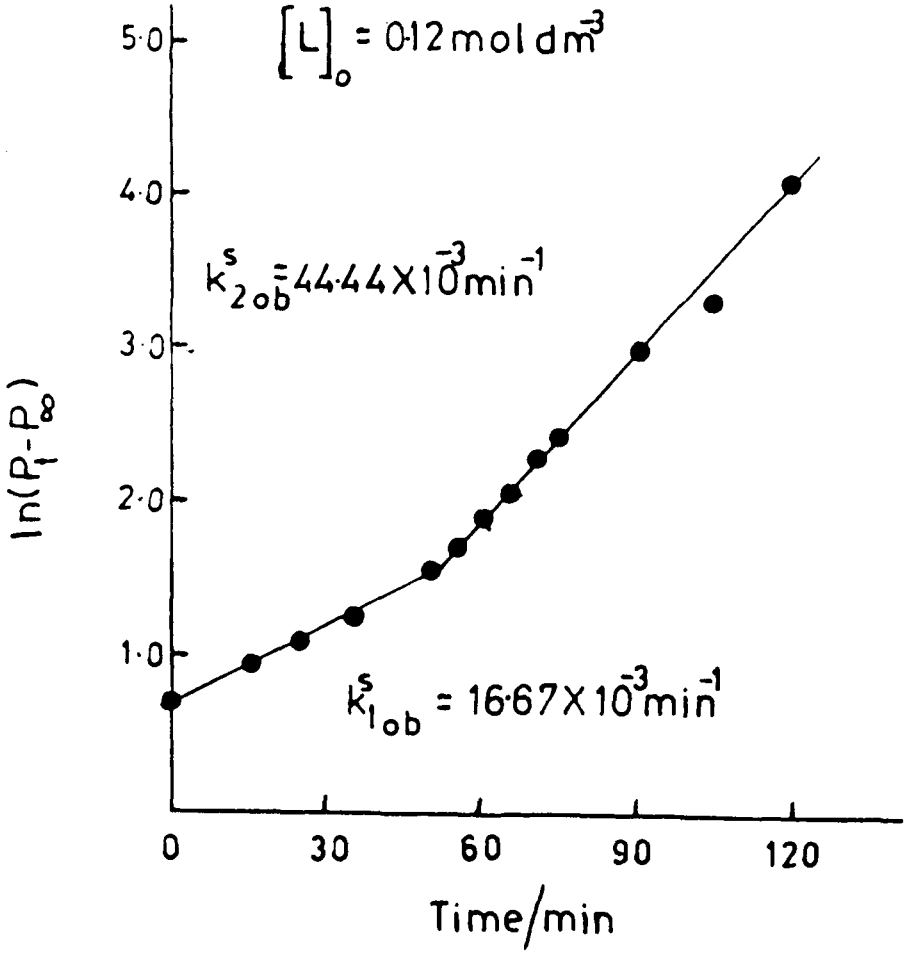


Figure4d

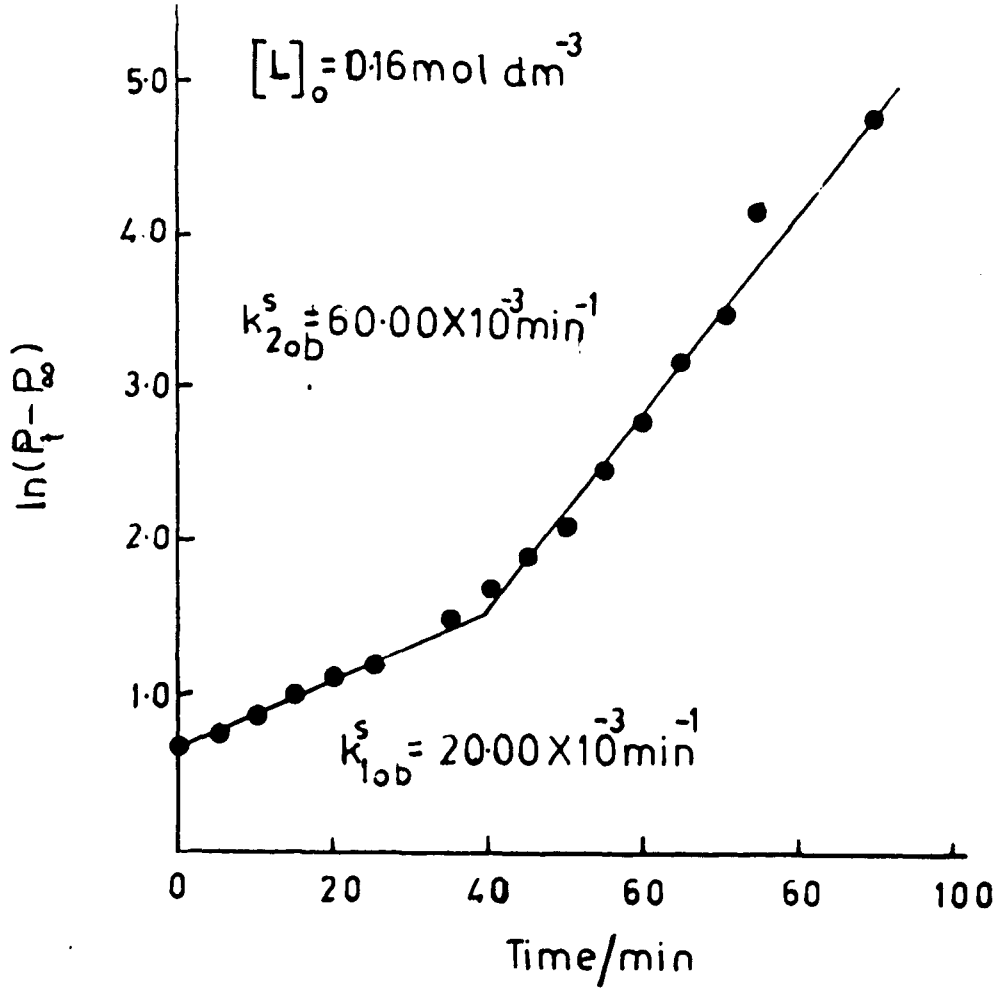


Figure4e

Plot of $\ln(P_t - P_\infty)$ VS time in the presence of SDS

Temp = 30°C, $[H^+]$ = 0·20 mol dm⁻³, μ = 0·20 mol dm⁻³,

$[MnO_4^-] = 2 \times 10^{-4}$ mol dm⁻³, [SDS] = 0·10 mol dm⁻³

Table 10 to 12 + Figure 5a to 5l

Showing effect of the $[H^+]$ on the observed rate constant (k^s_{1ob} and k^s_{2ob}).

Table-10 : Effect of the $[H^+]$ on absorbance at 530 nm in the presence of SDS.

$[H^+]$	0.20M	0.15M	0.10M	0.05M
Time	absorbance at 530 nm			
0	0.475	0.475	0.475	0.475
15	0.400	0.415	0.415	0.430
30	0.370	0.375	0.375	0.375
45	0.340	0.340	0.330	0.320
60	0.315	0.305	0.295	0.260
75	0.280	0.265	0.250	0.195
90	0.250	0.225	0.200	0.145
105	0.220	0.195	0.165	0.100
120	0.185	0.155	0.130	0.070
135	0.155	-	0.100	0.050
150	0.135	0.095	0.075	0.035
165	-	-	0.060	0.030
180	0.090	0.060	0.045	0.020
195	-	-	0.035	0.015
210	0.050	0.035	0.025	0.010
225	-	-	0.025	0.010
240	0.035	0.020	0.015	0.010
255	-	-	0.015	
270	0.025	0.015	0.015	
300	0.020	0.015		
330	0.020			

Temp. = $30^{\circ}C$, $[L]_o$ = 0.02 mol dm^{-3}, μ = 0.20 mol dm^{-3}, $[MnO_4^-]$ = 2×10^{-4} mol dm^{-3}, [SDS] = 0.01 mol dm^{-3}.

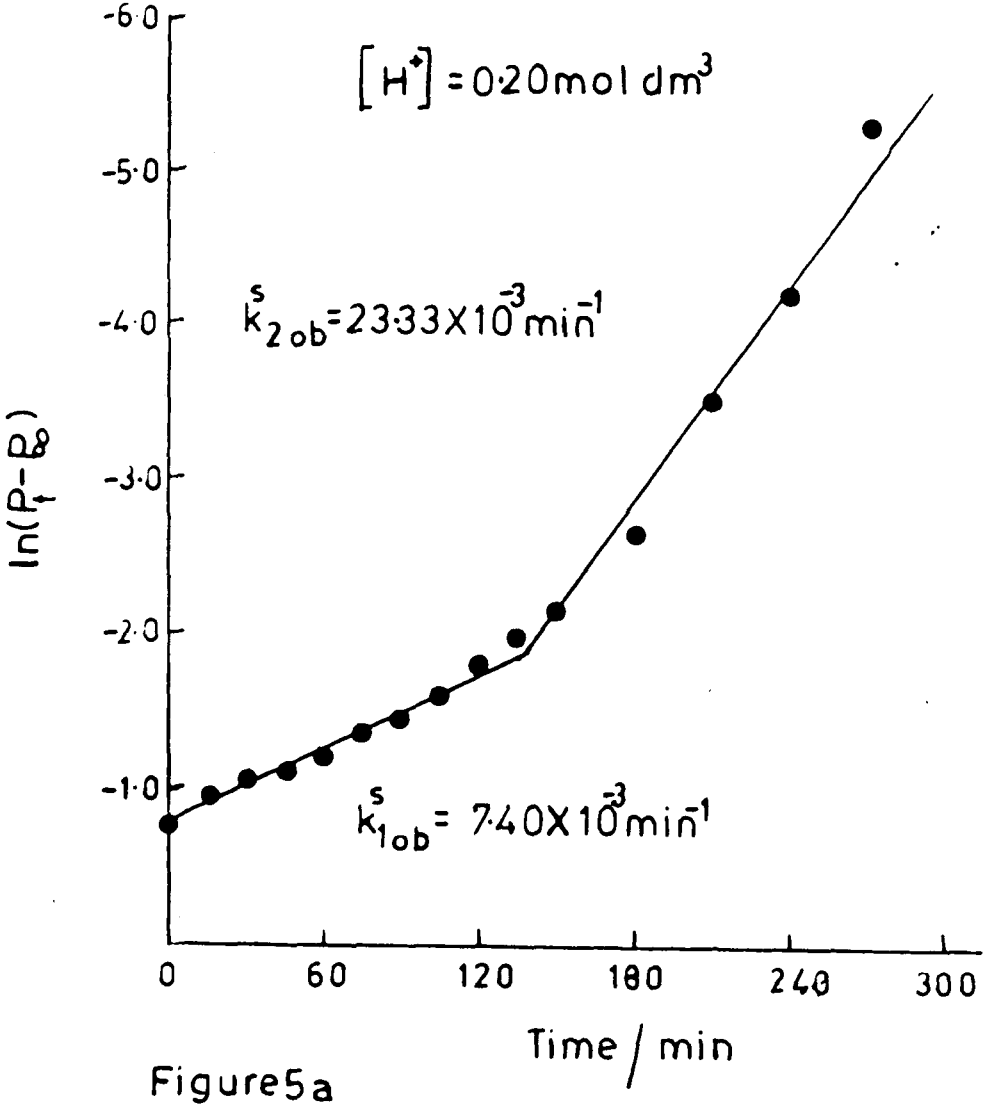


Figure5a

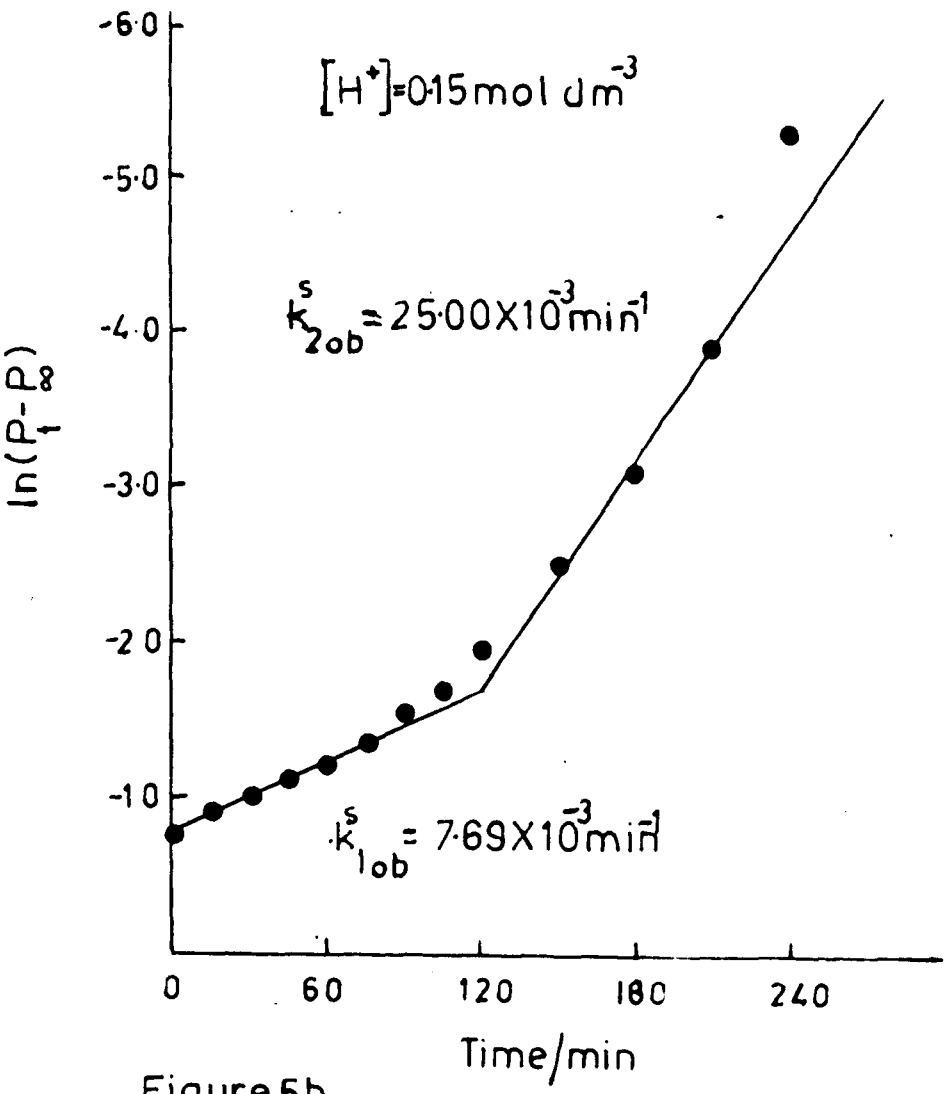


Figure 5b

Plot of $\ln(P_t - P_\infty)$ VS time in the presence of SDS

Temp= 30°C, $[L]_0$=0·02mol dm^{-3}, μ = 0·20 mol dm^{-3},

$[MnO_4^-]$ = 2X10^{-4}mol dm^{-3}, [SDS] = 0·01mol dm^{-3}

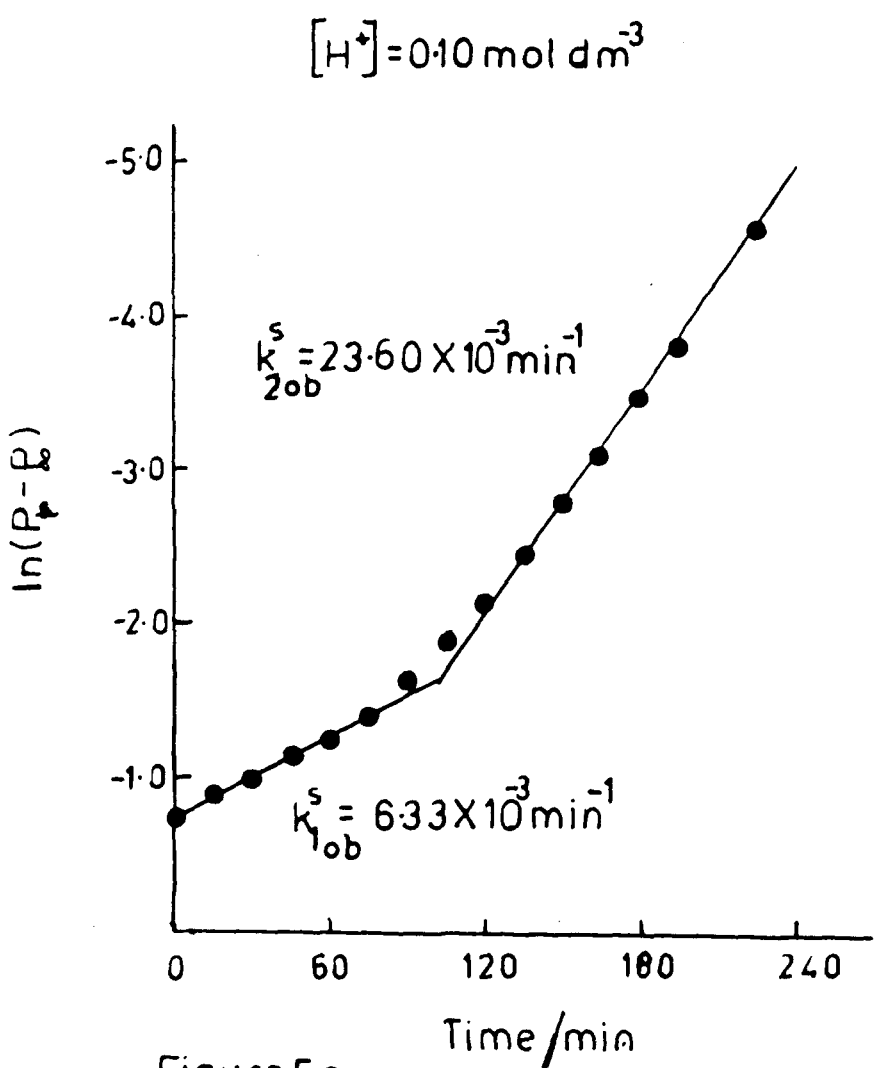


Figure 5c

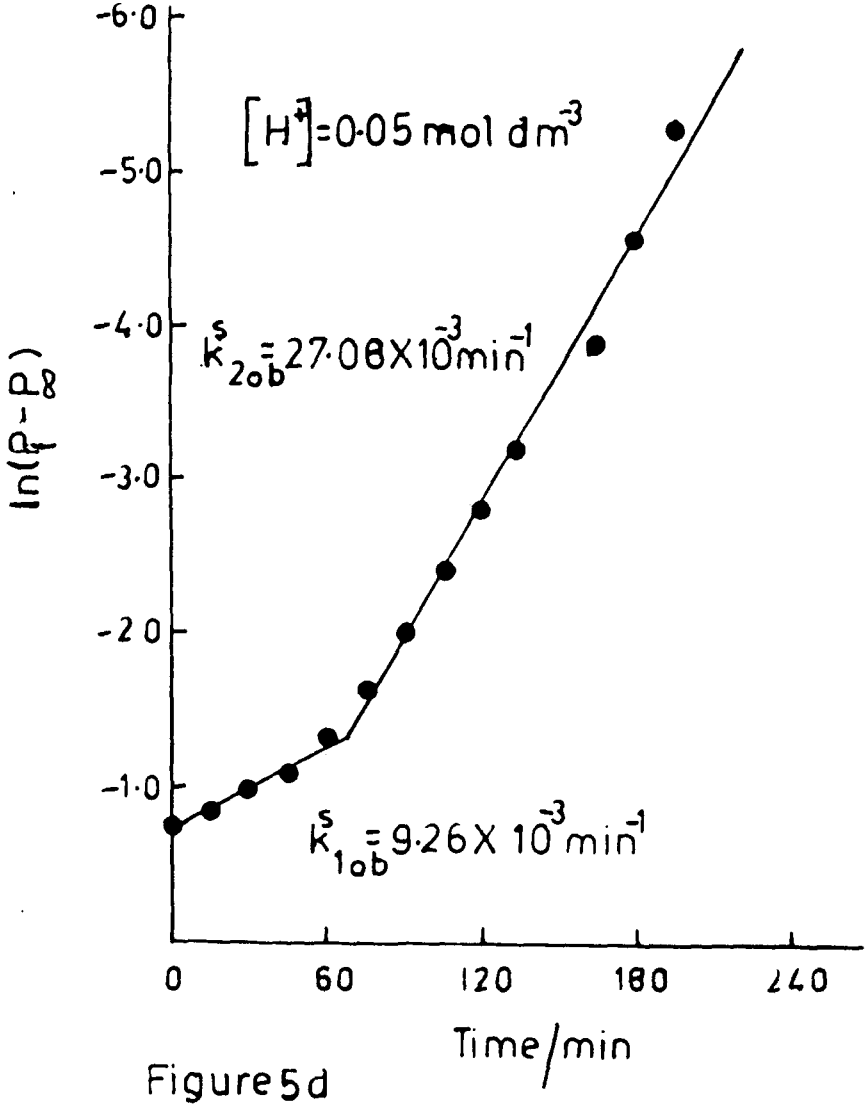


Figure 5d

Plot of $\ln(P_t - P_\infty)$ VS time in the presence of SDS

Temp = 30°C, $[L]_o$ = 0·02 mol dm^{-3}, μ = 0·20 mol dm^{-3},

$[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS] = 0·01 mol dm^{-3}

Table-11 : Effect of the $[H^+]$ on the absorbance at 530 nm in the presence of SDS.

$[H^+]$	0.20M	0.15M	0.10M	0.05M
Time	absorbance at 530 nm			
0	0.480	0.440	0.480	0.480
15	0.445	0.410	0.425	0.415
30	0.410	0.375	0.370	0.350
45	0.360	0.335	0.325	0.300
60	0.325	0.305	0.285	0.245
75	0.300	0.265	0.250	0.190
90	0.265	0.230	0.195	0.140
105	0.230	0.195	0.155	0.095
120	0.195	0.160	0.125	0.070
135	0.160	0.125	0.095	0.045
150	0.140	0.090	0.075	0.030
165	0.100	0.070	-	-
180	0.075	0.060	0.045	0.015
195	0.060	0.050	-	-
210	0.050	0.040	0.025	0.010
225	-	0.025	-	-
240	0.030	0.020	0.010	0.010
270	0.025	0.010	0.010	
300	0.015	0.010		
330	0.015			

Temp. = 30°C, $[L]_o$ = 0.04 mol dm^{-3}, μ = 0.20 mol dm^{-3}, $[MnO_4^-]$ = 2×10^{-4} mol dm^{-3}, [SDS] = 0.01 mol dm^{-3}.

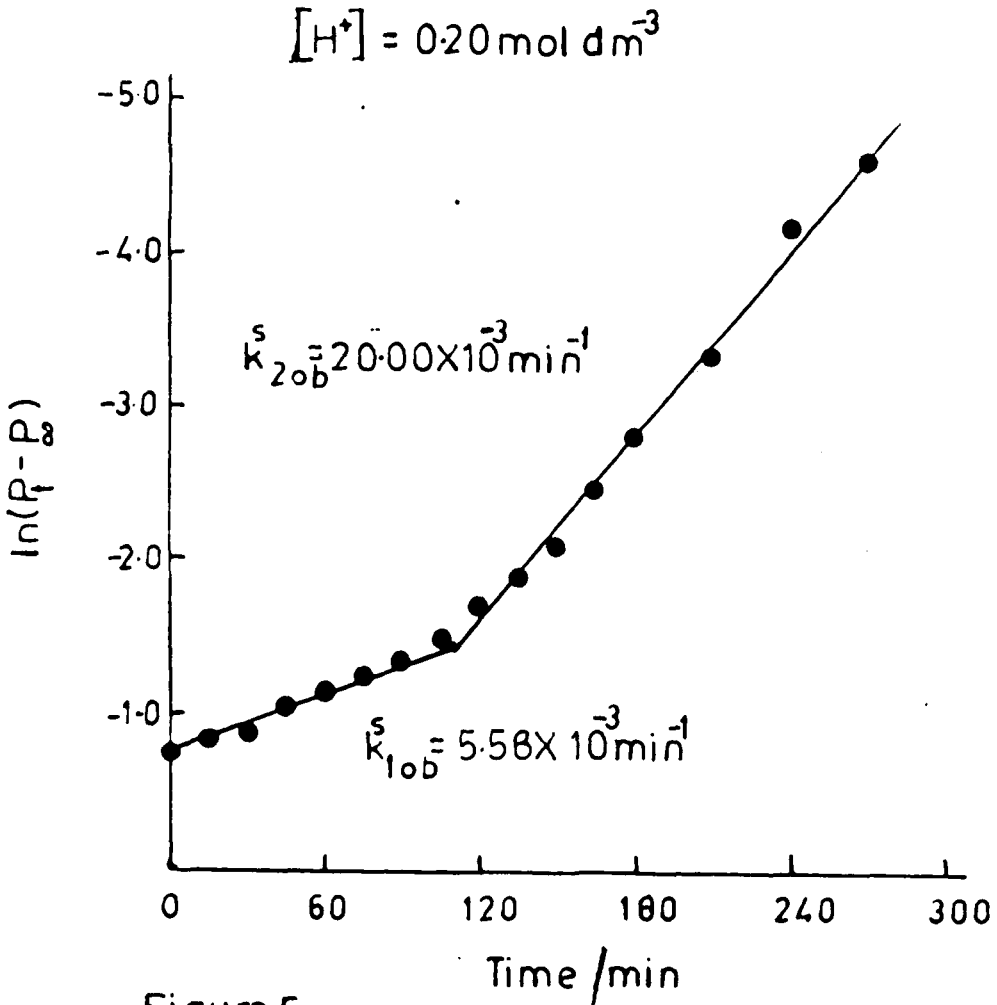
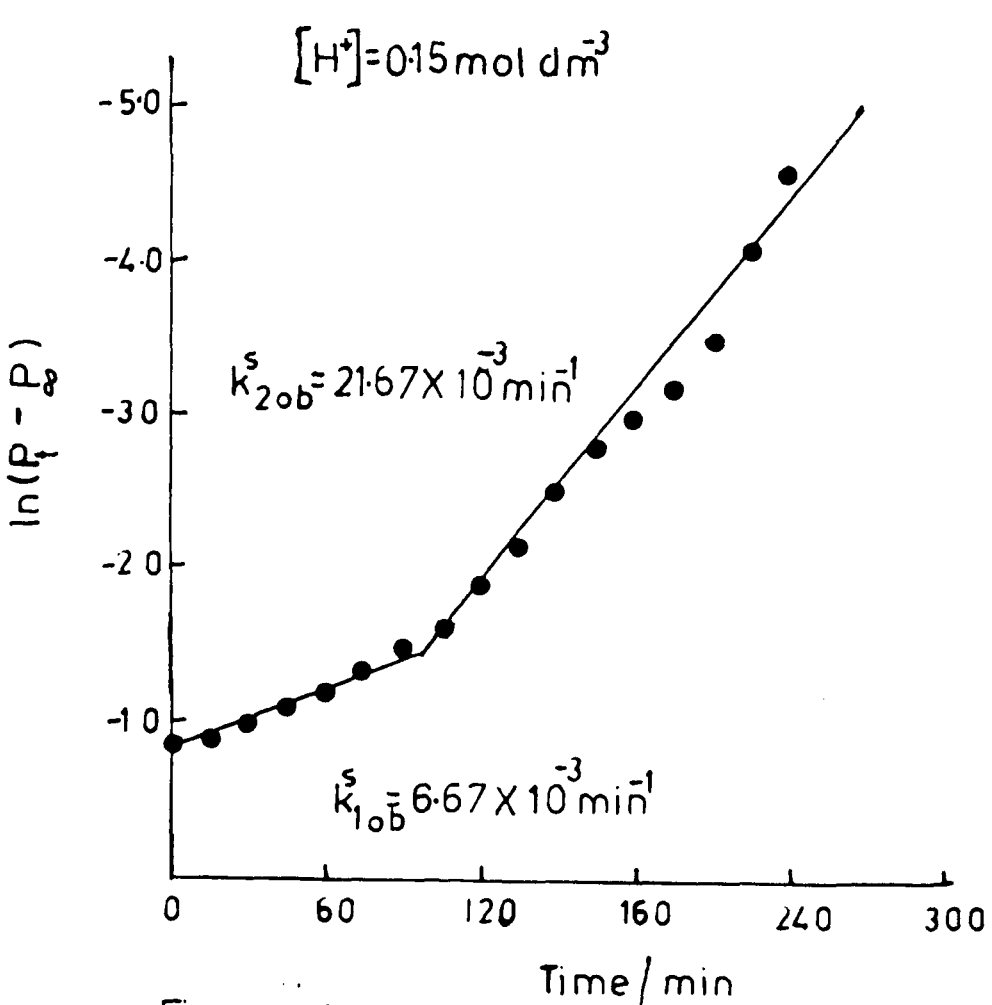


Figure 5e



Figrue 5 f

Plot of $\ln(P_t - P_\infty)$ VS time in the presence of SDS

Temp = 30°C, $[L]_o$ = 0·04 mol dm^{-3}, μ = 0·20 mol dm^{-3}

$[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS] = 0·01 mol dm^{-3}

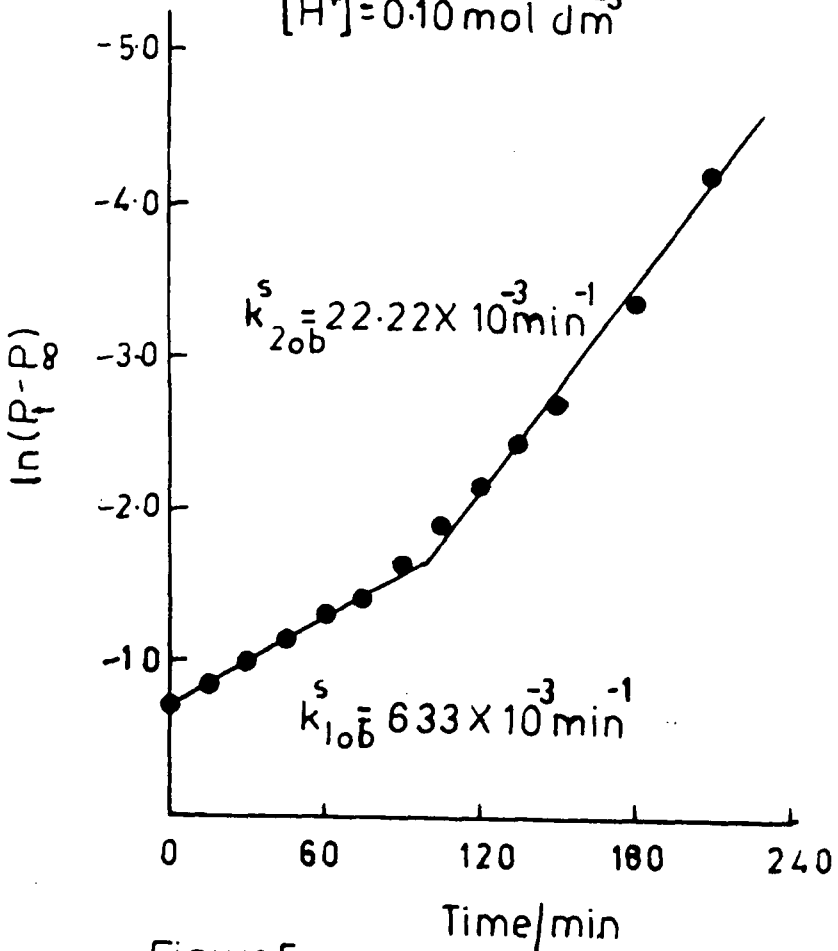


Figure 5g

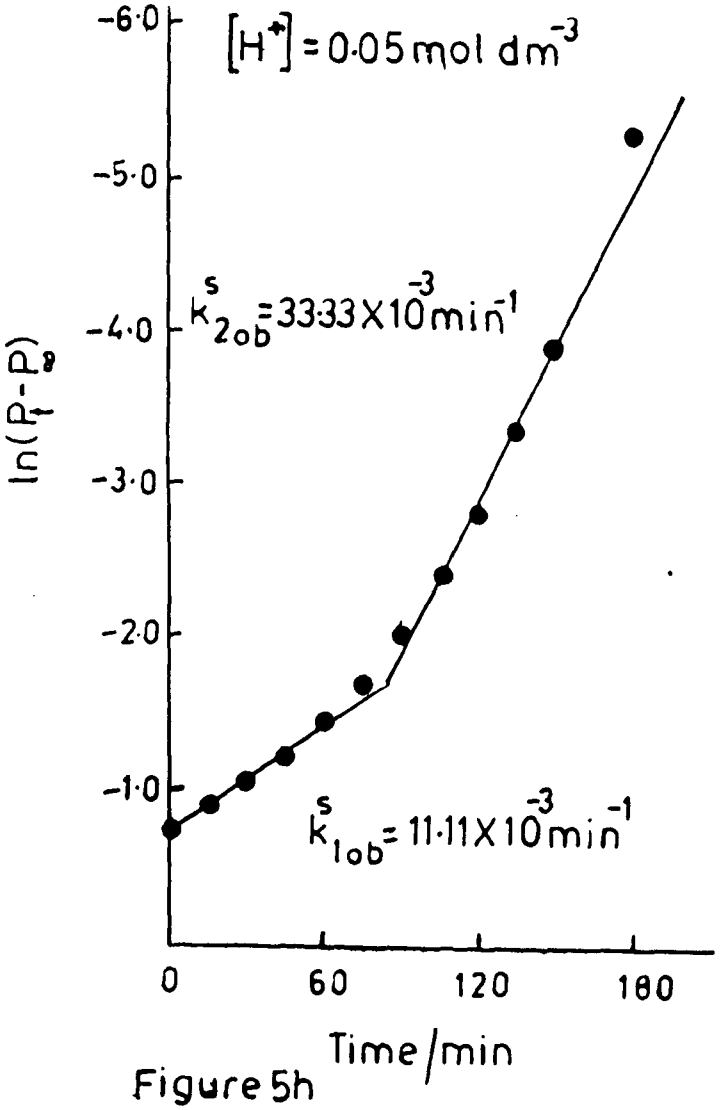


Figure 5h

Plot of $\ln(P_t - P_\infty)$ VS time in the presence of SDS

Temp = 30°C, $[L]_o$ = 0·04 mol dm^{-3}, μ = 0·20 mol dm^{-3}

$[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS] = 0·01 mol dm^{-3}

Table-12 : Effect of the $[H^+]$ on absorbance at 530 nm in the presence of SDS.

$[H^+]$	0.20M	0.15M	0.10M	0.05M
Time	absorbance at 530 nm			
0	0.485	0.485	0.485	0.485
15	0.390	0.385	0.385	0.385
30	0.355	0.340	0.315	0.290
45	0.315	0.295	0.255	0.200
60	0.270	0.245	0.210	0.125
75	0.230	0.205	0.160	0.090
90	0.195	0.170	0.120	0.045
105	0.165	0.140	0.095	0.035
120	0.135	0.110	0.070	0.030
135	-	0.090	0.060	0.020
150	0.075	0.060	0.045	0.010
180	0.040	0.030	0.020	0.010
210	0.025	0.010	0.010	
240	0.015	0.010	0.010	
270	0.010			
300	0.010			

Temp. = 30^oC, $[L]_o$ = 0.08 mol dm^{-3}, μ = 0.20 mol dm^{-3}
$[MnO_4^-]$ = 2×10^{-4} mol dm^{-3}, [SDS] = 0.01 mol dm^{-3}.

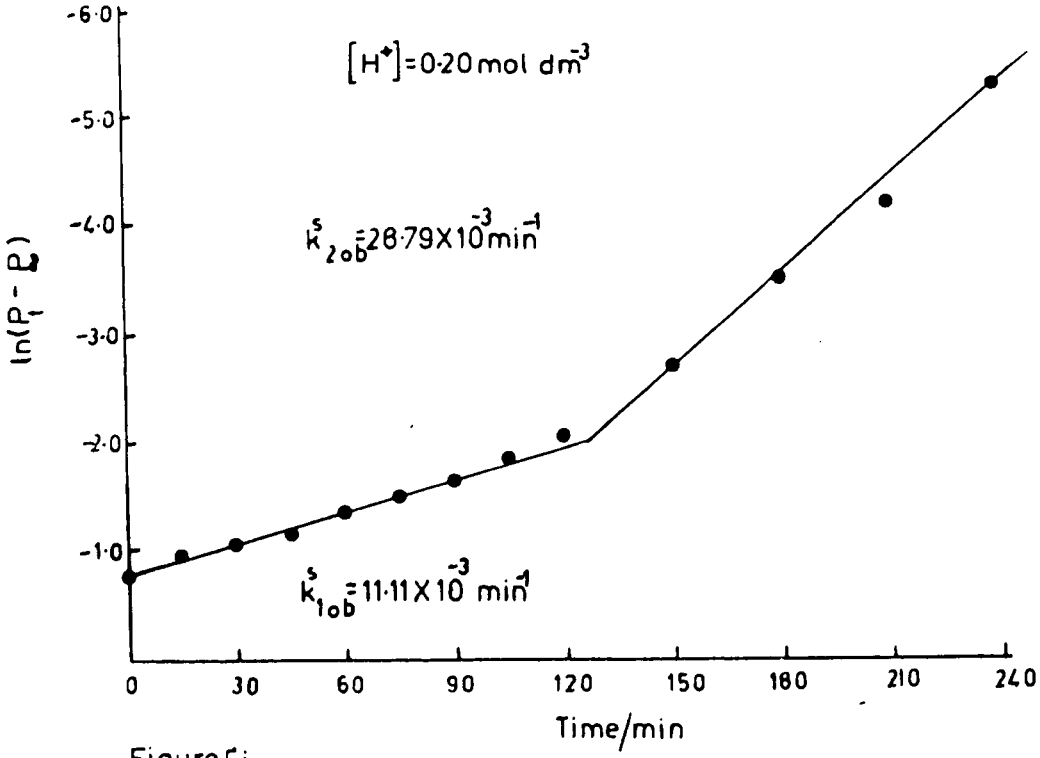


Figure 5i

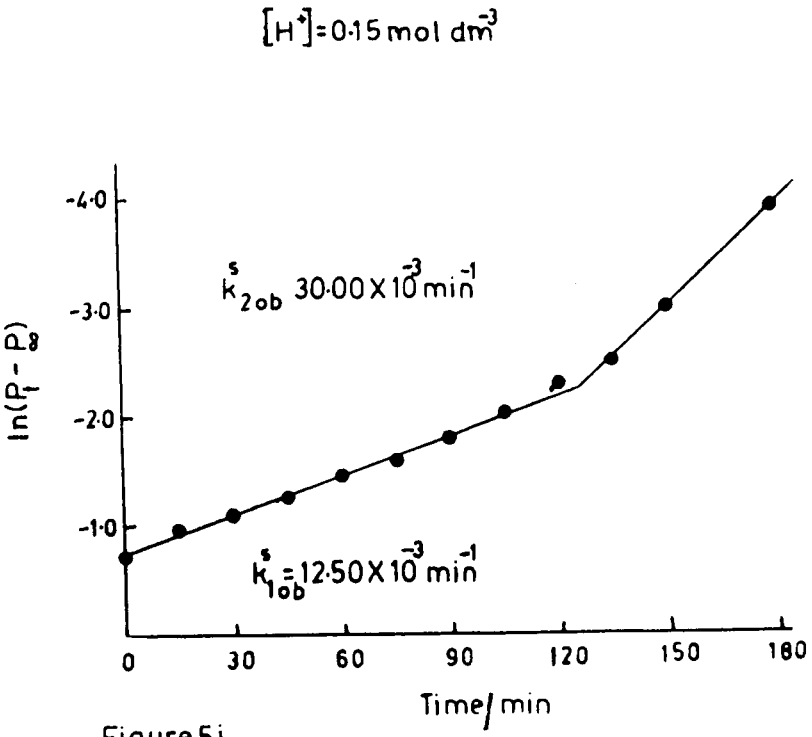


Figure 5j

Plot of $\ln(P_t - P_\infty)$ VS time in the presence of SDS

Temp = 30°C, $[L]_o$ = 0·08 mol dm^{-3}, μ = 0·20 mol dm^{-3},

$[MnO_4^-]$ = 2X10^{-4} mol dm^{-3}, [SDS] = 0·01 mol dm^{-3}

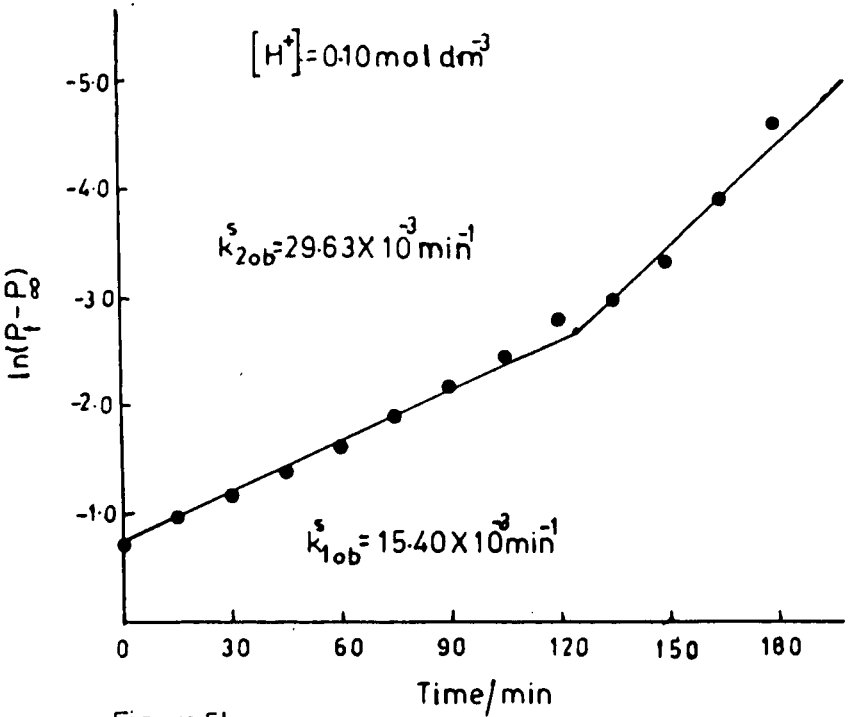


Figure 5k

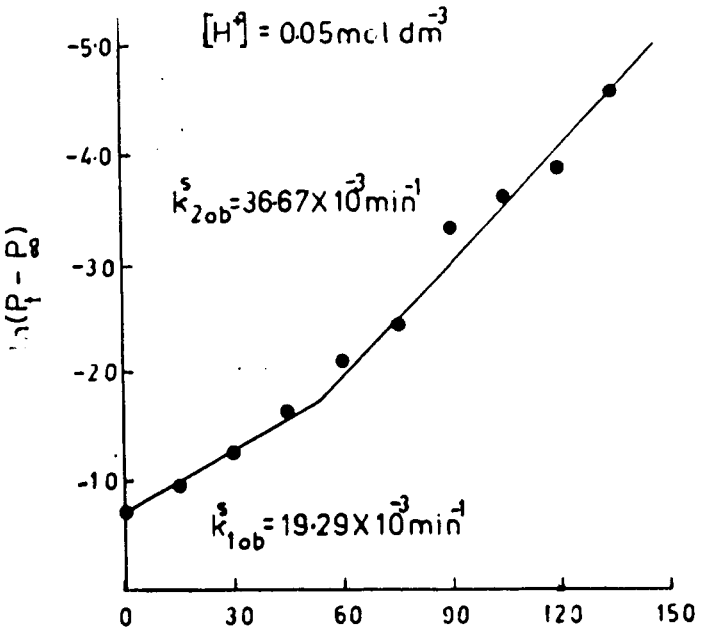


Figure 5l

Plot of $\ln(P_t - P_\infty)$ VS time in the presence of SDS
Temp = 30°C, $[L]_o$ = 0·08mol dm^{-3}, μ = 0·20mol dm^{-3},
$[MnO_4^-]$ = 2X10^{-4}mol dm^{-3}, [SDS] = 0·01mol dm^{-3}

Table 13 to 15 + Figure 6a to 6i

Showing effect of temperature on the observed rate constant (k^{s}_{1ob} and k^{s}_{2ob}).

Table-13 : Effect of temperature on absorbance at 530 nm in the presence of SDS

Lysine	0.02M	0.04M	0.08M
Time	absorbance at 530 nm		
0	0.505	0.485	0.485
15	0.475	0.455	0.430
30	0.450	0.420	0.385
45	0.415	0.395	0.355
60	0.370	0.360	0.320
75	0.345	0.345	0.290
90	0.315	0.315	0.260
105	0.295	0.285	0.235
120	0.275	0.265	0.205
135	0.250	0.235	–
150	0.225	0.215	0.160
165	—	0.190	0.140
180	0.180	0.170	0.120
195	0.160	0.150	0.100
210	0.150	0.135	0.080
225	0.135	—	–
240	0.115	0.110	0.060
270	0.100	0.080	0.040
300	0.085	0.060	0.020
330	0.060	0.040	0.020
360	0.050	0.030	
390	0.040	0.030	
420	0.040		
450	0.040		

Temp. = 30°C, $[H^+]$ = 0.20 mol dm^{-3}, μ = 0.20 mol dm^{-3}, $[MnO_4^-]$ = 2×10^{-4} mol dm^{-3}, [SDS] = 0.01 mol dm^{-3}.

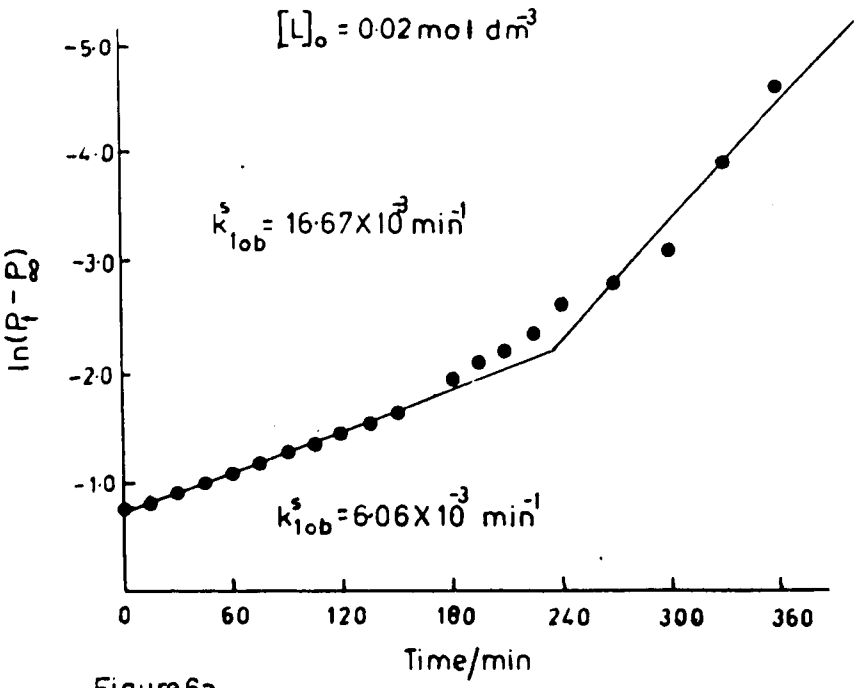


Figure 6a

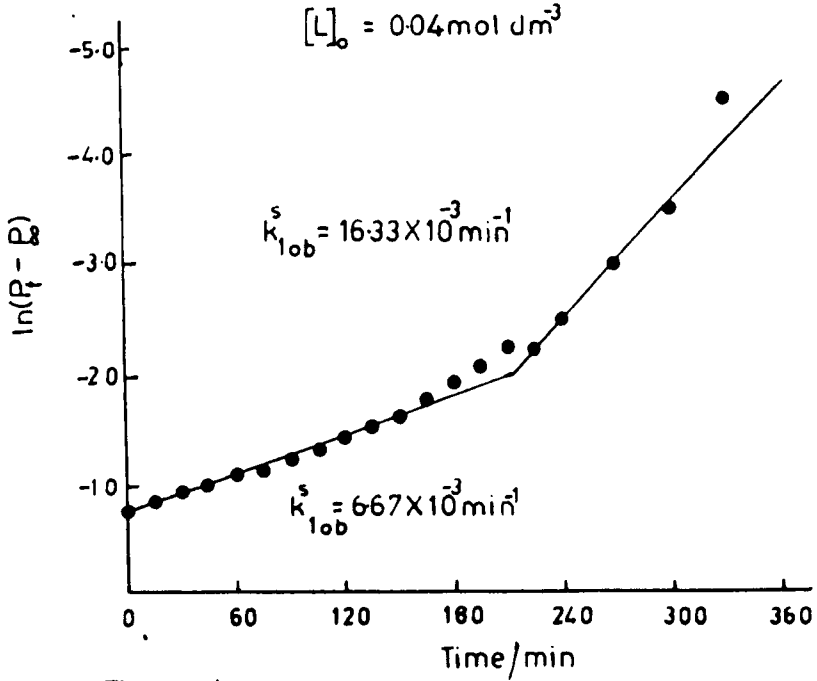


Figure 6b

Plot of ln(P$_t$ - P$_\infty$) VS time in the presence of SDS

Temp = 30°C, $[H^+]$ = 0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3},

$[MnO_4^-]$ = 2X10^{-4} mol dm^{-3}, [SDS] = 0·01 mol dm^{-3}

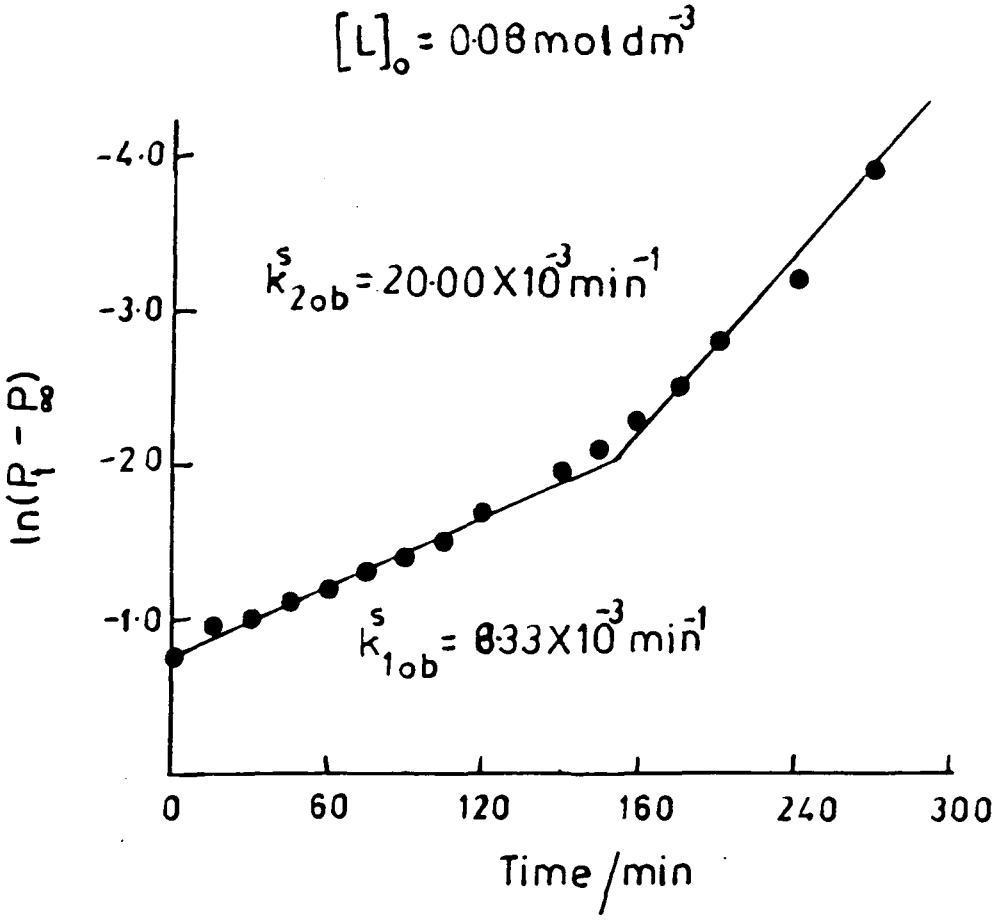


Figure 6c Plot of $\ln(P_t - P_\infty)$ VS time in the presence of SDS
Temp = 30°C, $[H^+] = 0{\cdot}20\,mol\,dm^{-3}$, $\mu = 0{\cdot}20\,mol\,dm^{-3}$
$[MnO_4^-] = 2 \times 10^{-4}\,mol\,dm^{-3}$, $[SDS] = 0{\cdot}01\,mol\,dm^{-3}$

Table-14 : Effect of temperature on absorbance at 530 nm in the presence of SDS.

Lysine	0.02M	0.04M	0.08M
Time	absorbance at 530 nm		
0	0.495	0.485	0.485
15	0.470	0.450	0.390
30	0.440	0.400	0.355
45	0.405	0.375	0.315
60	0.375	0.335	0.270
75	0.340	0.305	0.230
90	0.300	0.270	0.195
105	0.275	0.240	0.165
120	0.225	0.200	0.135
135	-	0.160	0.110
150	0.185	0.140	0.075
165	-	0.100	-
180	0.115	0.075	0.040
195	0.090	0.050	-
210	0.065	0.040	0.020
240	0.050	0.030	0.015
270	0.040	0.020	0.010
300	0.030	0.015	0.010
330	0.030	0.015	-

Temp. = $35^{o}C$, $[H^{+}]$ = 0.20 mol dm^{-3}, μ = 0.20 mol dm^{-3}
$[MnO_4^-]$ = 2×10^{-4} mol dm^{-3}, [SDS] = 0.01 mol dm^{-3}.

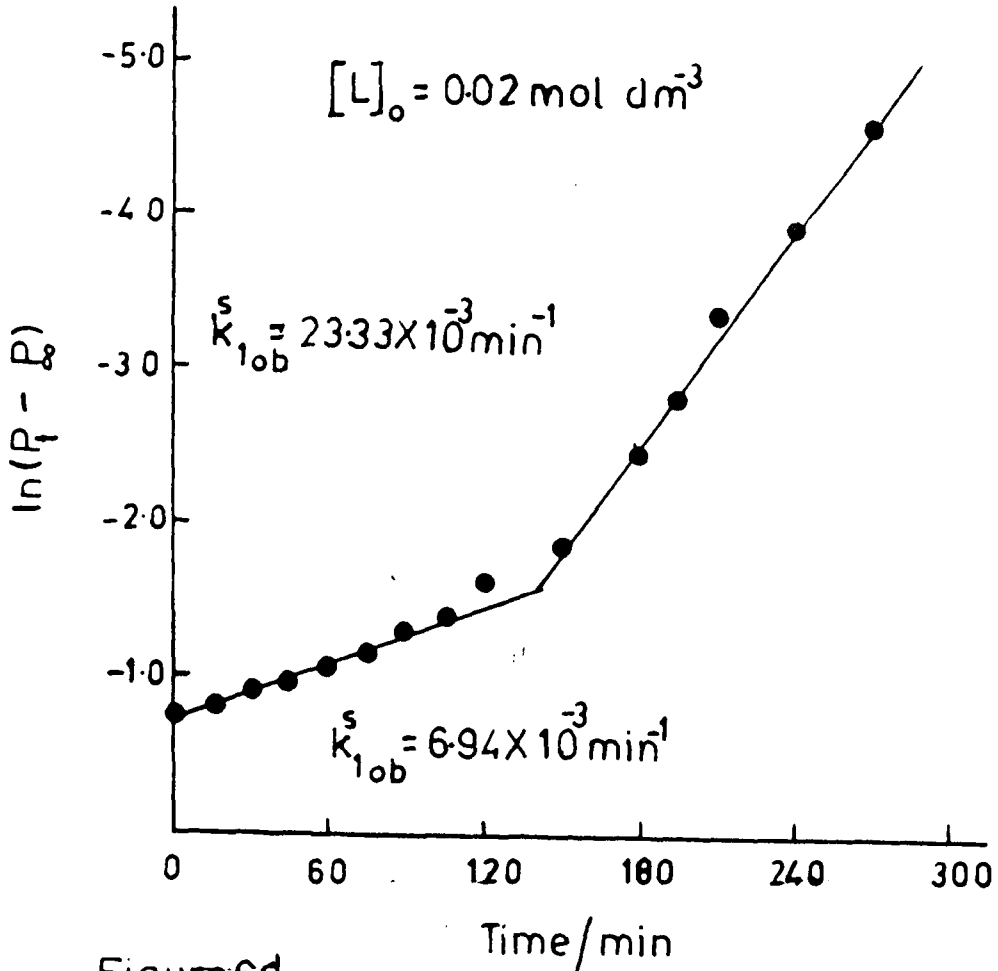


Figure 6d

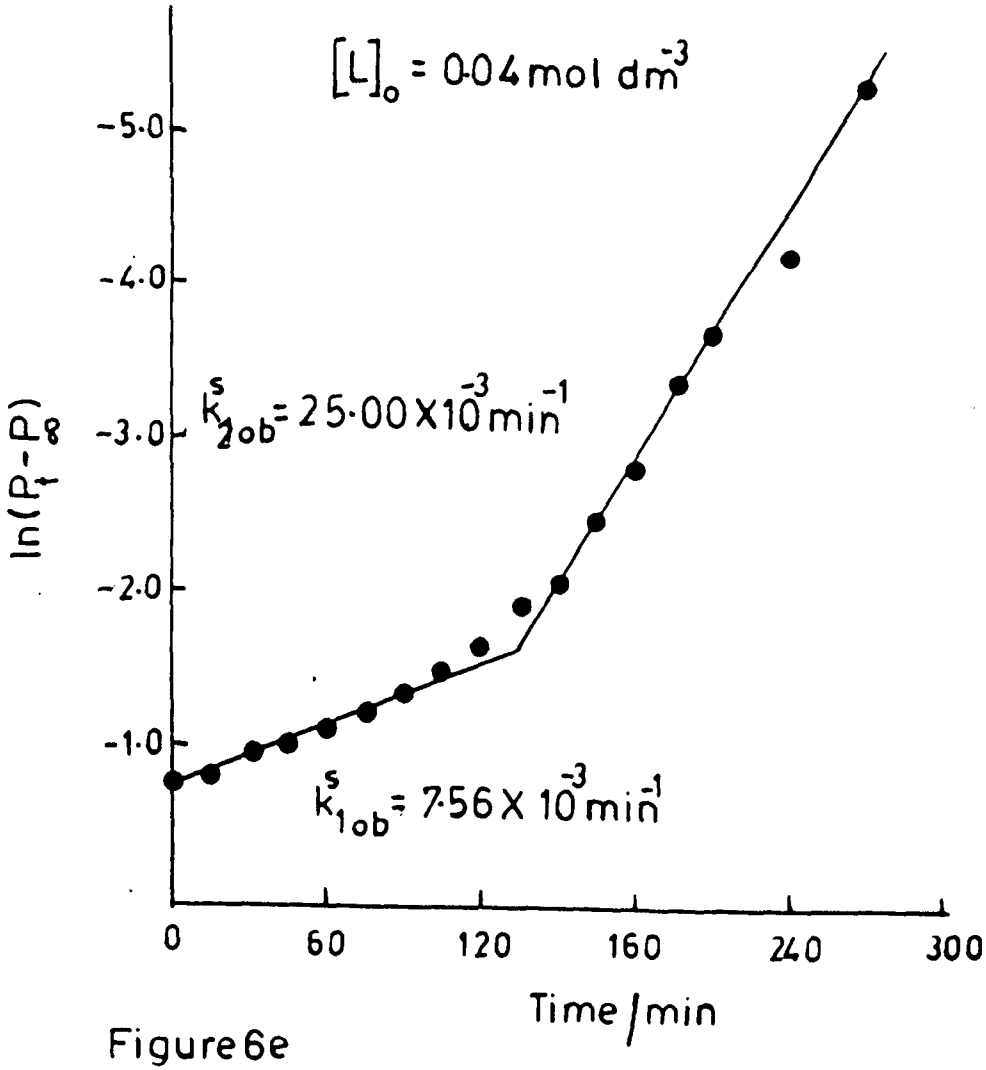


Figure 6e

Plot of $\ln(P_t - P_\infty)$ VS time in the presence of SDS

Temp = 35°C, $[H^+] = 0.20\ mol\ dm^{-3}$, $\mu = 0.20\ mol\ dm^{-3}$,

$[MnO_4^-] = 2 \times 10^{-4}\ mol\ dm^3$, $[SDS] = 0.01\ mol\ dm^{-3}$

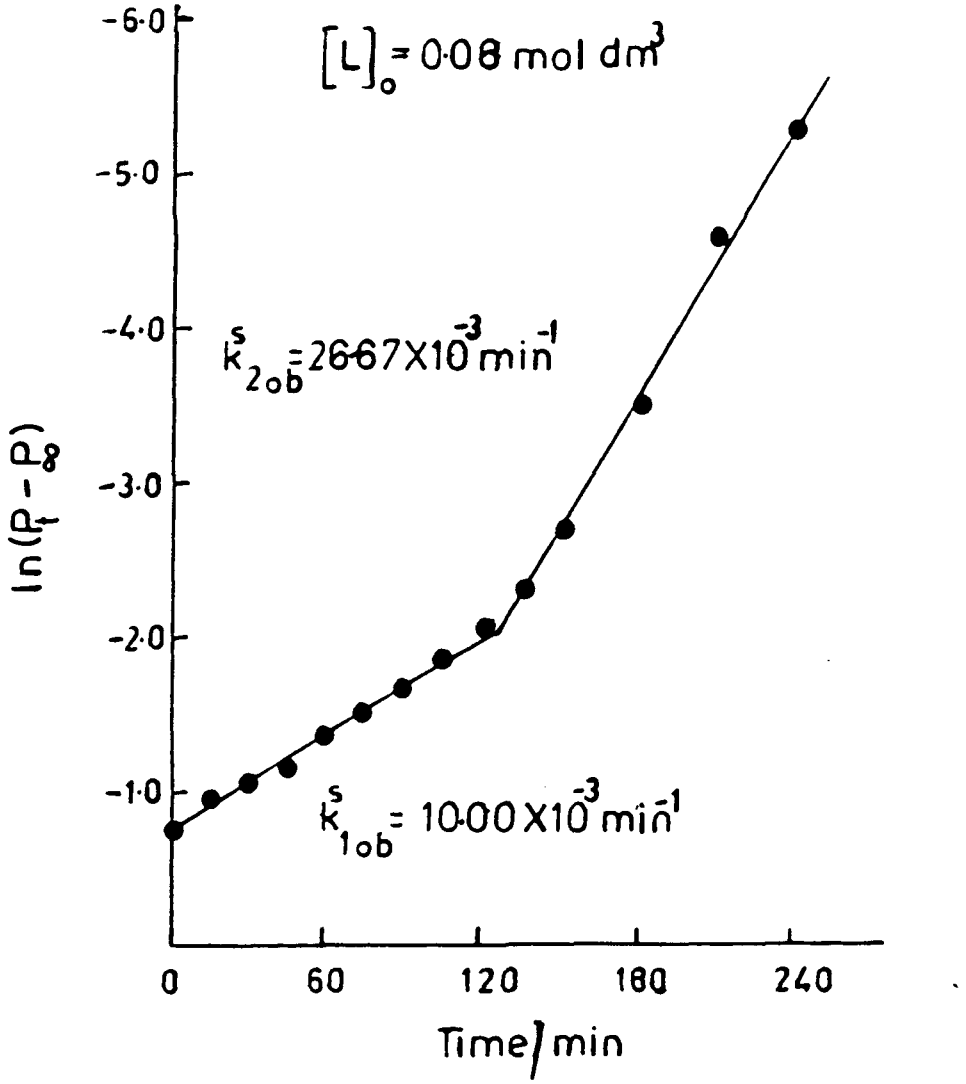


Figure 6f Plot of $\ln(P_t - P_\infty)$ VS time in the presence of SDS
Temp = 35°C, $[H^+] = 0.20$ mol dm^{-3}, $\mu = 0.20$ mol dm^{-3}
$[MnO_4^-] = 2 \times 10^{-4}$ mol dm^{-3}, $[SDS] = 0.01$ mol dm^{-3}.

Table-15 : Effect of temperature on absorbance at 530 nm in the presence of SDS.

Lysine	0.02M	0.04M	0.08M
Time	absorbance at 530 nm		
0	0.500	0.490	0.480
15	0.450	0.400	0.360
30	0.400	0.355	0.315
45	0.350	0.300	0.260
60	0.310	0.245	0.205
75	0.250	0.200	0.160
90	0.200	0.155	0.115
105	0.155	0.115	0.080
120	0.115	0.080	0.050
135	0.075	0.050	0.030
150	0.050	0.030	0.020
165	0.035	-	0.015
180	0.030	0.020	0.010
210	0.025	0.015	-
240	0.020	0.015	-
270	0.020	-	-

Temp. = 40°C, $[H^+]$ = 0.20 mol dm^{-3}, μ = 0.20 mol dm^{-3}
$[MnO_4^-]$ = 2×10^{-4} mol dm^{-3}, [SDS] = 0.01 mol dm^{-3}.

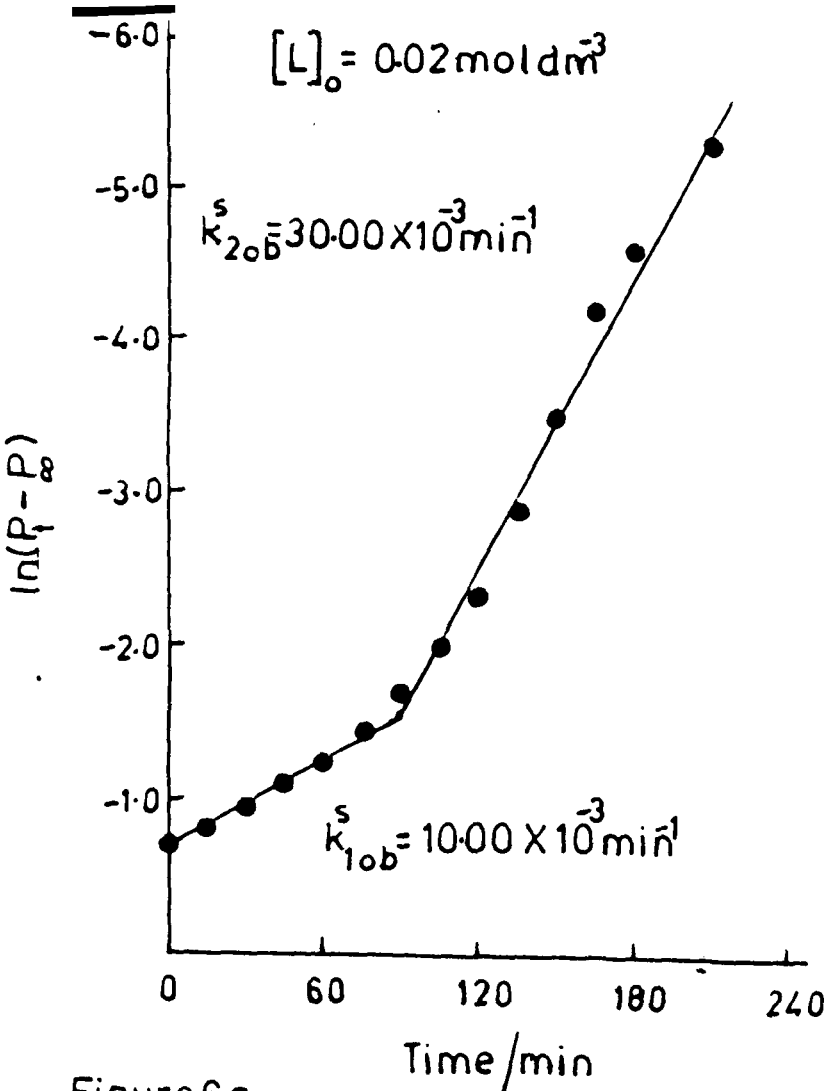


Figure 6g

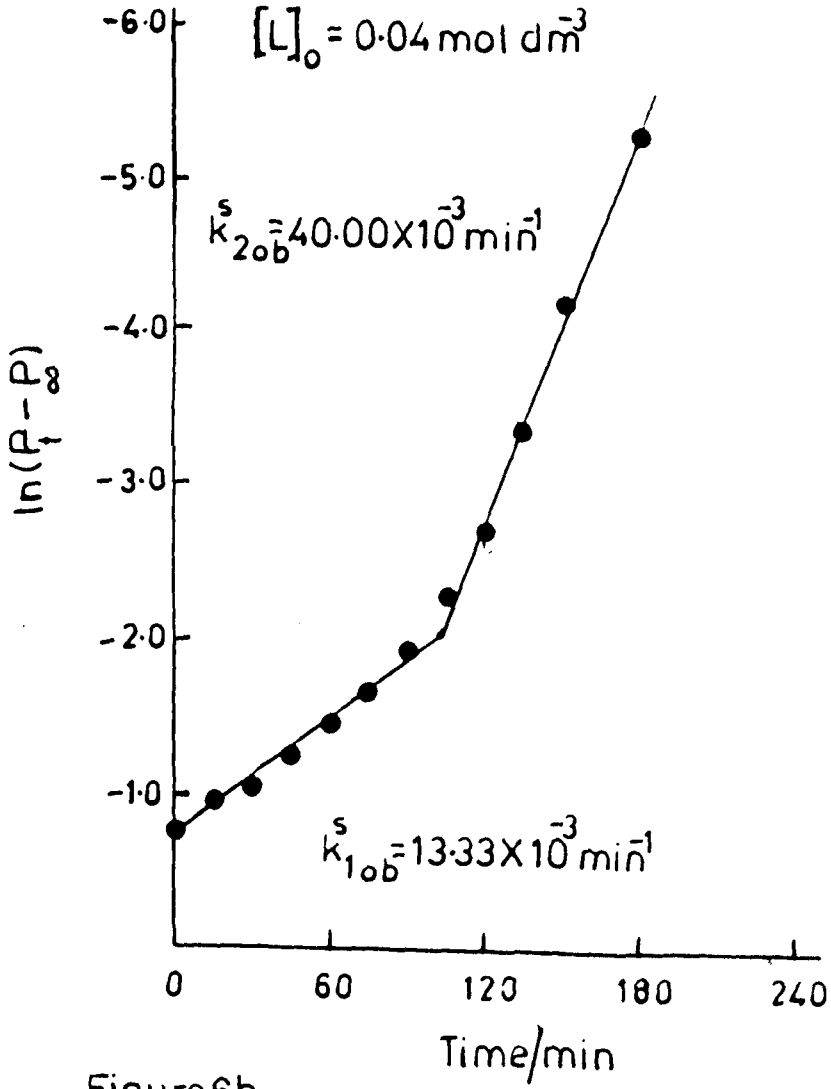


Figure 6h

Plot of $\ln(P_t - P_\infty)$ VS time in the presence of SDS

Temp = 40°C, $[H^+]$ = 0.20 mol dm⁻³, μ = 0.20 mol dm⁻³,

$[MnO_4^-] = 2 \times 10^{-4}$ mol dm⁻³, [SDS] = 0.01 mol dm⁻³

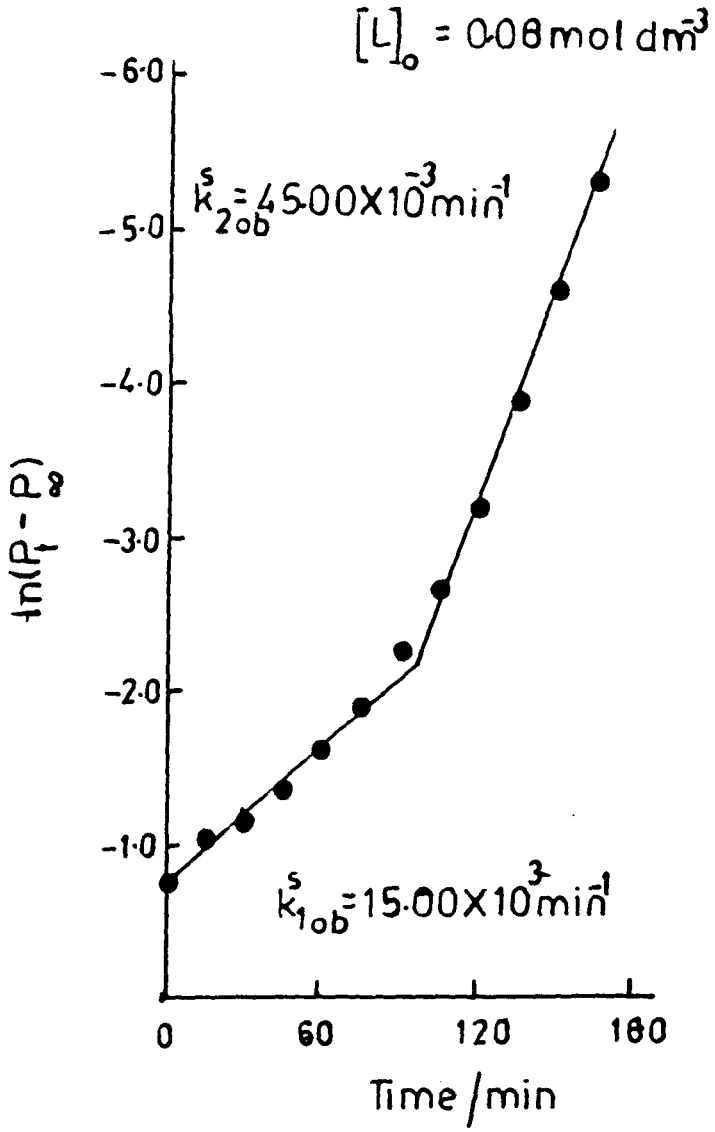


Figure 6i Plot of ln($P_t - P_\infty$) VS time in presence of SDS
Temp = 40°C, $[H^+]$ = 0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3},
$[MnO_4^-]$ = 2 X 10^{-4} mol dm, [SDS] = 0·01 mol dm^{-3}

Table 16 + Figure 7a to 7d

Showing effect of the [SDS] on the observed rate constant (k^{s}_{1ob} and k^{s}_{2ob}).

Table-16 : Effect of the concentration of SDS on absorbance at 530 nm.

[SDS]	0.01M	0.02M	0.03M	0.04M
Time	absorbance at 530 nm			
0	0.485	0.450	0.410	0.375
15	0.450	0.340	0.265	0.200
30	0.400	0.300	0.200	0.130
45	0.375	0.245	0.145	0.070
60	0.335	0.200	0.095	0.040
75	0.305	0.155	0.065	0.025
90	0.270	0.105	0.045	-
105	0.240	-	-	0.015
120	0.200	0.055	0.030	0.015
135	0.160	-	-	-
150	0.140	0.035	0.020	
165	0.100	-	0.020	
180	0.075	0.020		
195	0.050	0.020		
210	0.040			
240	0.030			
270	0.020			
300	0.015			
330	0.015			

Temp. = 30°C, $[H^+]$ = 0.20 mol dm^{-3}, μ = 0.20 mol dm^{-3}

$[MnO_4^-]$ = 2×10^{-4} mol dm^{-3}, $[L]_o$ = 0.04 mol dm^{-3}.

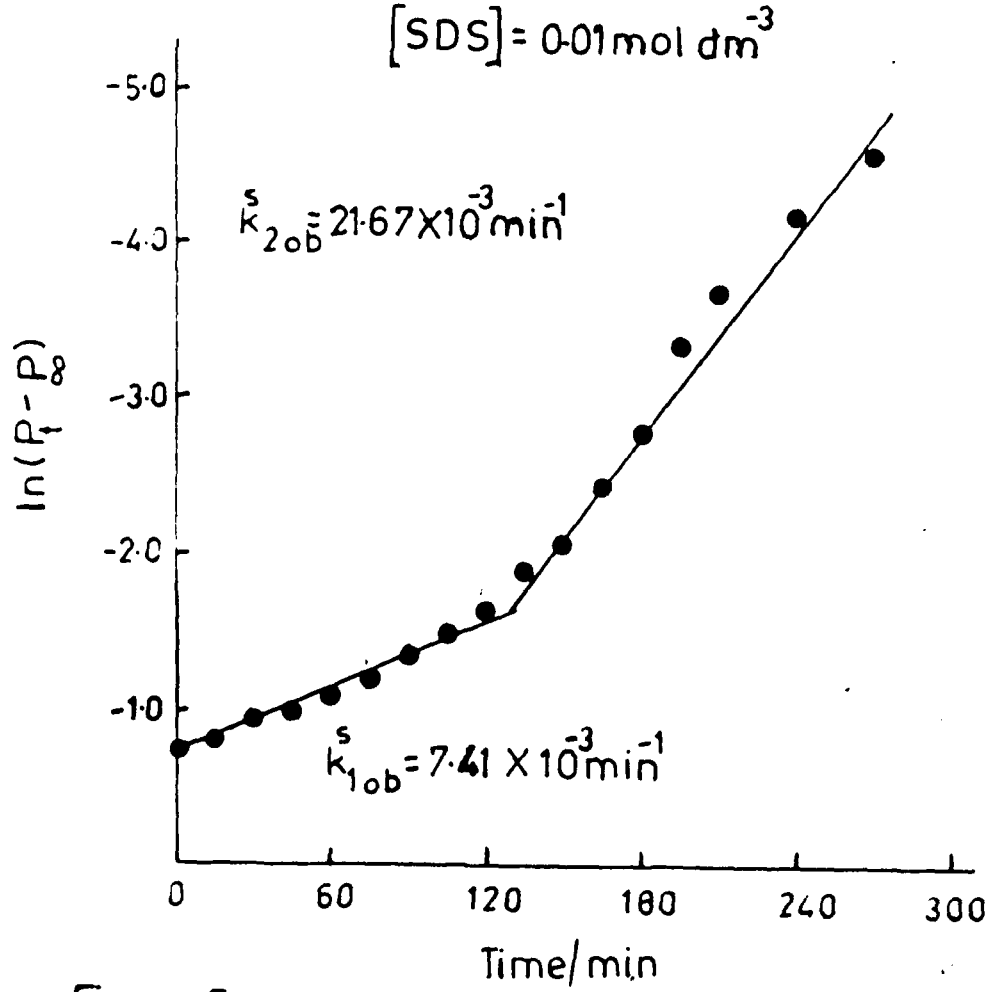


Figure 7a

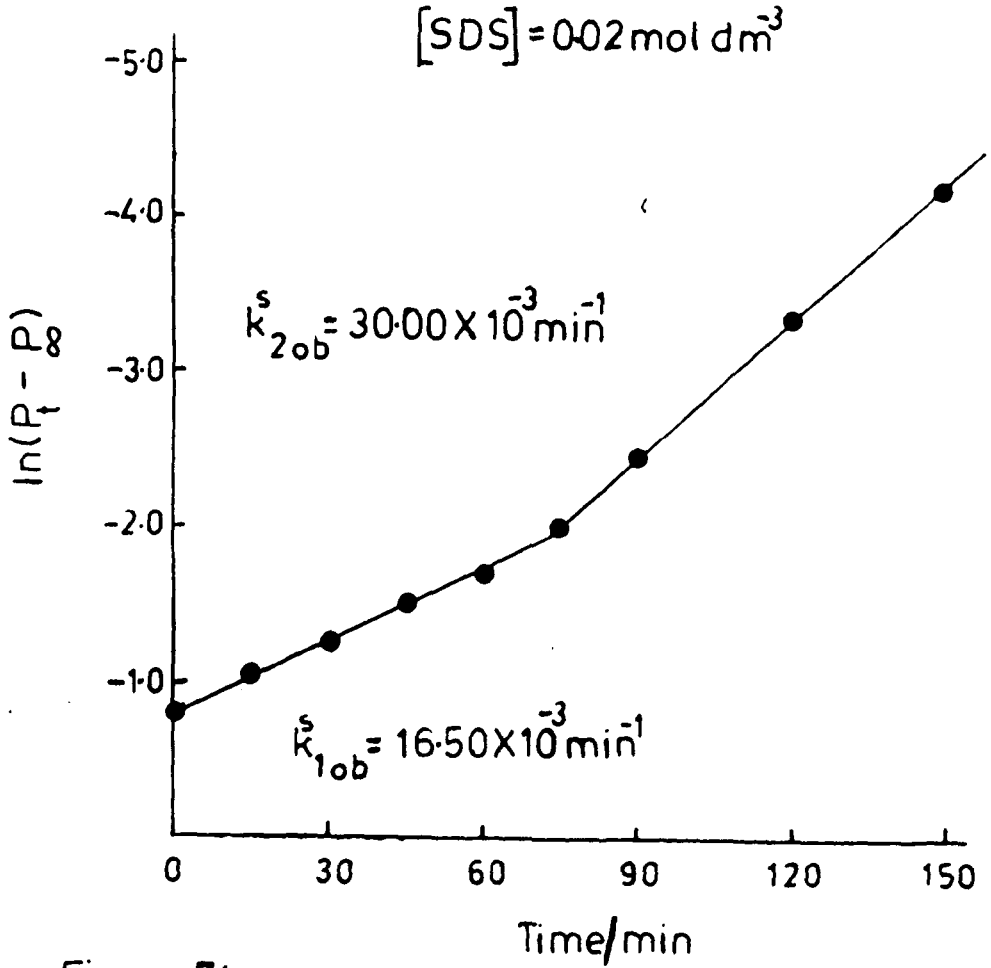


Figure 7b

Plot of $\ln(P_t - P_\infty)$ VS time

Temp = 30°C, $[H^+] = 0·20$ mol dm^{-3}, $\mu = 0·20$ mol dm^{-3}

$[MnO_4^-] = 2 \times 10^{-4}$ mol dm^{-3}, $[L]_o = 0·04$ mol dm^{-3}

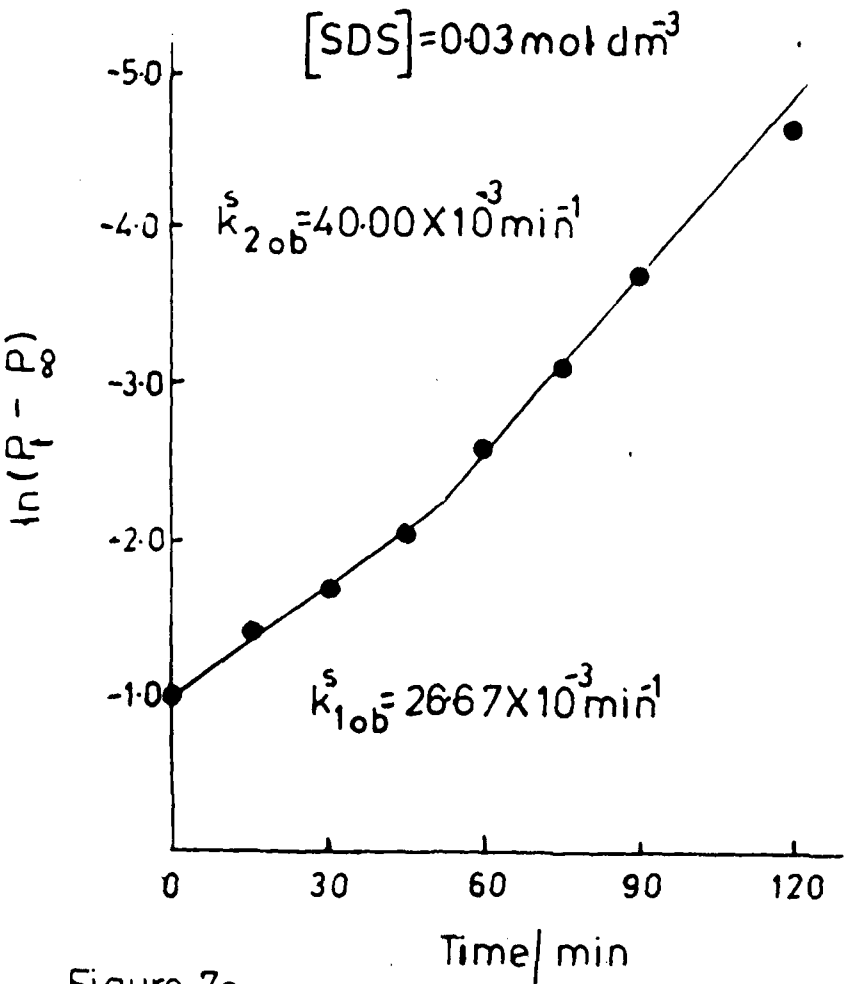


Figure 7c

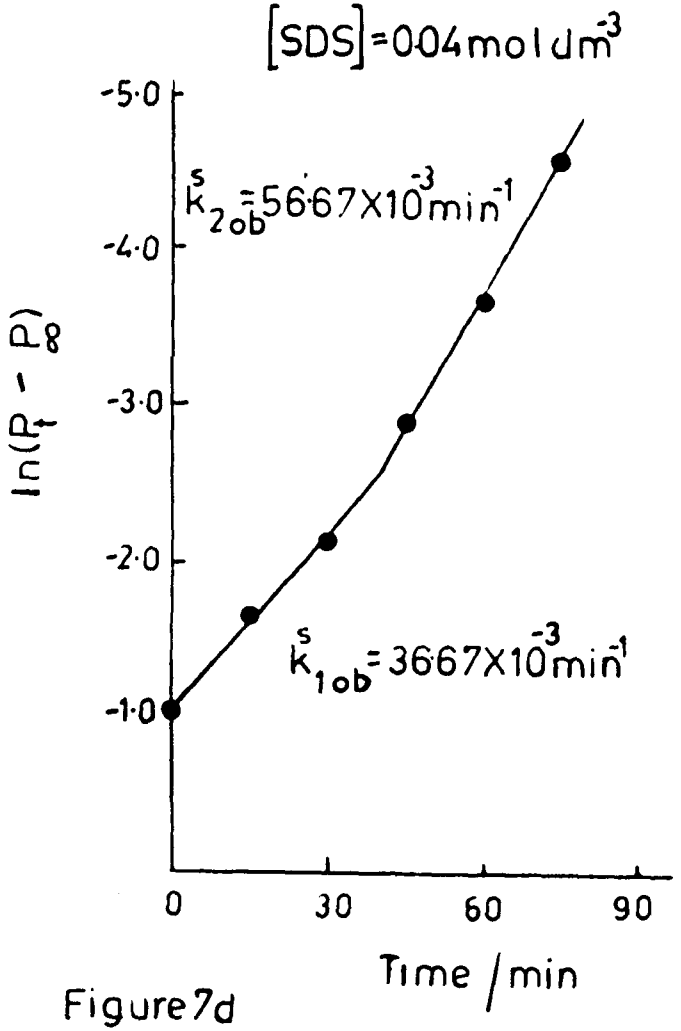


Figure 7d

Plot of $\ln(P_t - P_\infty)$ VS time

Temp=30°C, $[H^+]$=0·20 mol dm⁻³, μ = 0·20 mol dm⁻³,

$[MnO_4^-]$ = 2X10⁻⁴ mol dm, $[L]_o$ = 0·04 mol dm⁻³

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

In the acid medium Lysine [L] is assumed to be completely protonated [LH^+]. It is also safe to assume that permanganate is completely dissociated in the reaction medium. The reaction kinetics of oxidative degradation of lysine appears to follow a two-phase kinetics because the plot of ln ($P_t - P_\infty$) (P_t and P_∞ are absorbance values at time t and after completion of the reaction respectively) vs time is found to give a break under all the experimental condition. In the initial stages the reaction is slow and follows pseudo first order kinetics whereas in the later stages the reaction becomes the rapid and autocatalyzed. It appears that manganes (II) is responsible for the autocatalysis. The slopes of the plot ln ($P_t - P_\infty$) vs time give the pseudo first order rate constants k_{1ob} and k_{2ob} respectively. The dependence of k_{1ob} and k_{2ob} on other reaction parameters such as lysine concentration, hydrogen ion concentration and temperature have been investigated. The dependence of the rate constant k_{1ob} on [lysine] and [H^+] show a complex kinetics. It is found that the plots of $1/k_{ob}$ vs $1/[L]_o$ and $1/k_{1ob}$ vs [H^+] are linear. These feature in the background a two phase kinetic model has been proposed as under.

(A) Mechanism and Kinetics of the slow phase :

Mechanism :

$L + H^+ \longrightarrow LH^+$	...(1)	Lysine is completely protonated
$HP \longrightarrow P^- + H^+$	...(2)	Permanganic acid is completely ionized.
$LH^+ + P^- \overset{K_1}{\rightleftharpoons} LHP$	...(3)	Permanganate forms complex with protonated lysine.
$LHP \overset{K_2}{\rightleftharpoons} LP^- + H^+$	...(4)	Deprotonated complex LP^- is the reactive species.
$LP^- \xrightarrow{k} .....$	...(5)	Deprotonated complex decomposes unimolecularly.

Derivation of the rate expression

From the above mechanism the equilibrium K_1 and K_2 may be defined as

$$K_1 = \frac{[LHP]}{[LH^+][P^-]} \quad \text{and} \quad K_2 = \frac{[H^+][LP^-]}{[LHP]}$$

also,

$$K_{12} = K_1K_2 = \frac{[H^+][LP^-]}{[LH^+][P^-]}$$

At any time the total concentration of manganese(VII) present in different forms such as free permanganate ion $[P^-]$, lysine permanganate complex [LHP] and its deprotonated species $[LP^-]$ may be expressed as

$$[P_7] = [P^-] + [LHP] + [LP^-]$$

The concentration of the complex $[LP^-]$ may be obtained from the mass equation and equilibria K_1 and K_2,

$$[P_7] = \frac{[H^+][LP^-]}{K_{12}[LH^+]} + [LP^-] + \frac{[H^+][LP^-]}{K_2}$$

$$= \frac{K_2[H^+] + K_{212}[LH^+] + K_{12}[H^+][LH^+]}{K_{212}[LH^+]} \cdot [LP^-]$$

$$[LP^-] = \frac{K_{212}[P_7][LH^+]}{K_2[H^+] + K_{212}[LH^+] + K_{12}[H^+][LH^+]}$$

Using the above expression for the concentration of complex, LP^-, the rate expression may be obtained as under :

$$\text{rate} = k\,[LP^-]$$

$$= \frac{k\,K_{212}[LH^+]}{K_2[H^+] + K_{212}[LH^+] + K_{12}[LH^+][H^+]}$$

giving,

$$k_{lob} = \frac{k\,K_{212}[LH^+]}{K_2[H^+] + (K_2+[H^+])[LH^+].K_{12}} \qquad \ldots\ldots (6)$$

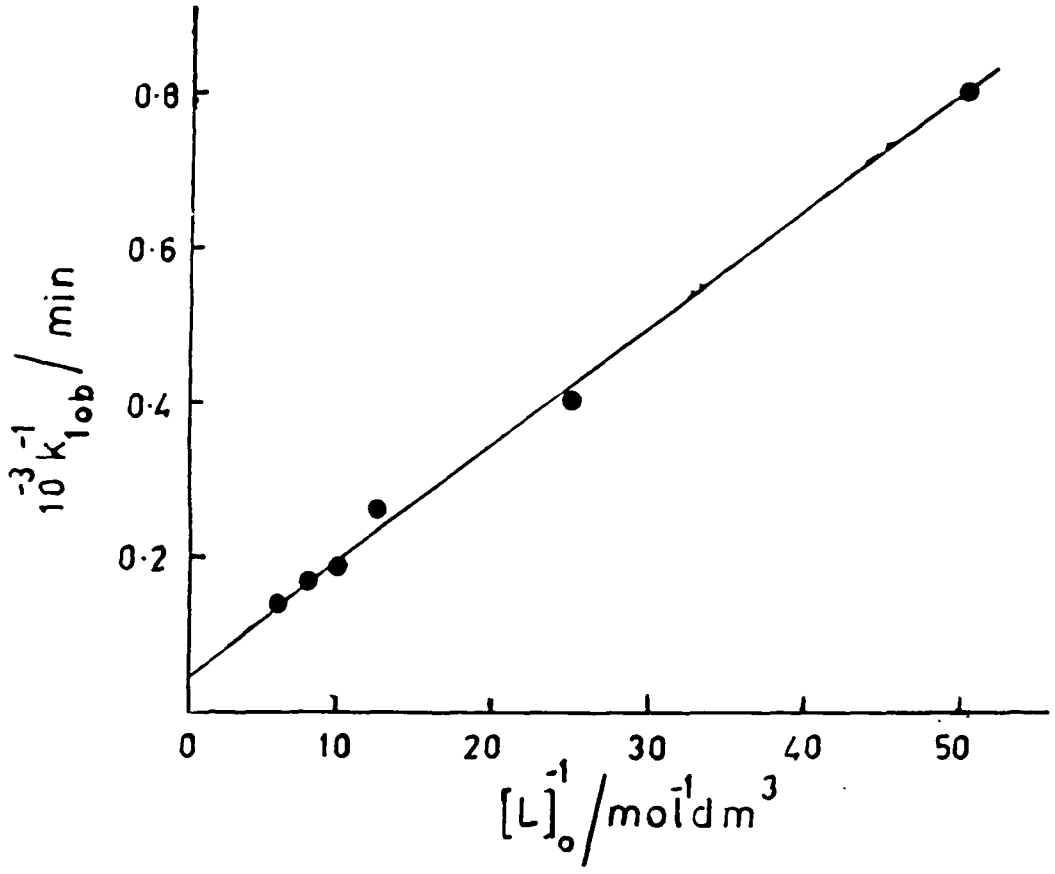


Figure 1 Plot of $1/k_{1ob}$ vs $1/[L]_o$ in the absence of SDS
Temp = 30°C, $[H^+]$ = 0·2 mol dm^{-3}, μ = 0·20 mol dm^{-3},
$[MnO_4^-]$ = 2×10^{-4} mol dm^{-3}, [SDS] = Nil

$$= \frac{k_1^o [LH^+]}{k_1' + k_1''[LH^+]} \qquad \ldots\ldots (7)$$

where,

$$k_1' = K_2[H^+]$$

$$k_1'' = K_{12}(K_2+[H^+])$$

$$k_1^o = kK_2K_{12}$$

$$K_{212} = K_2 \cdot K_{12}$$

Using equation (6) and (7) under different experimental conditions the relationship of the observed rate constant, k_{lob} and $[L]_o$ and relationship between k_{lob} and $[H^+]$ may be expressed as follows :

(a) At constant hydrogen ion concentration equation (7) gives,

$$k_{lob} = \frac{k_1^o [L]_o}{k_1' + k_1''[L]_o}$$

$$\frac{1}{k_{lob}} = \frac{k_1'}{k_1^o} \frac{1}{[L]_o} + \frac{k_1''}{k_1^o}$$

$$= \frac{K_2[H^+]}{kK_2K_{12}} \frac{1}{[L]_o} + \frac{K_{12}(K_2+[H^+])}{kK_2K_{12}}$$

$$\frac{1}{k_{lob}} = \frac{[H^+]}{kK_{12}} \frac{1}{[L]_o} + \frac{(K_2+[H^+])}{kK_2} \qquad \ldots\ldots (8)$$

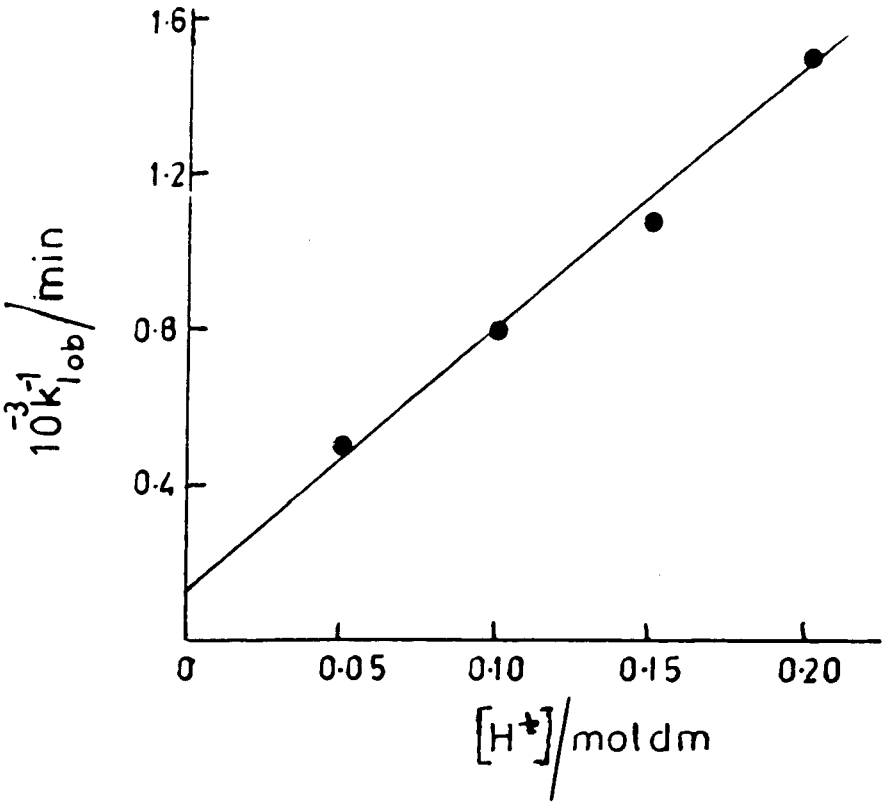


Figure 2a Plot of $1/k_{1ob}$ VS $[H^+]$ in the absence of SDS

Temp = 30°C, $[L]_o$ = 0·02 moldm^{-3}, μ = 0·20 moldm^{-3}, $[MnO_4^-]$ = 2×10^{-4} moldm^{-3}, $[SDS]$ = Nil

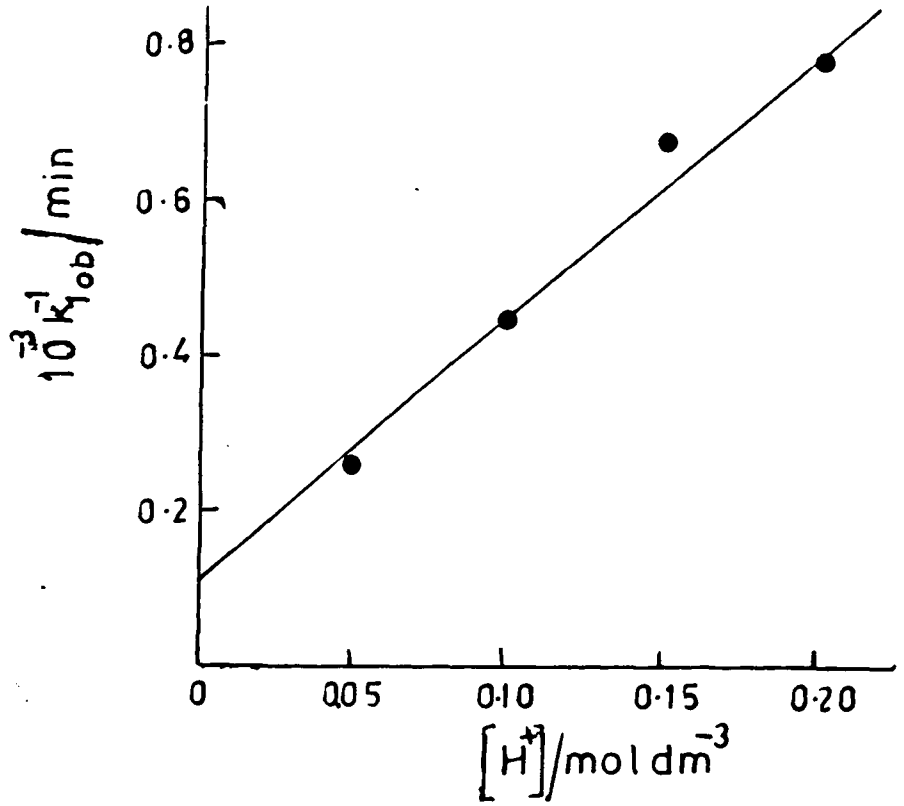


Figure 2b Plot of $1/k_{1ob}$ VS $[H^+]$ in the absence of SDS

Temp = 30°C, $[L]_o$ = 0·04 mol dm^{-3}, μ = 0·20 mol dm^{-3}

$[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS] = Nil

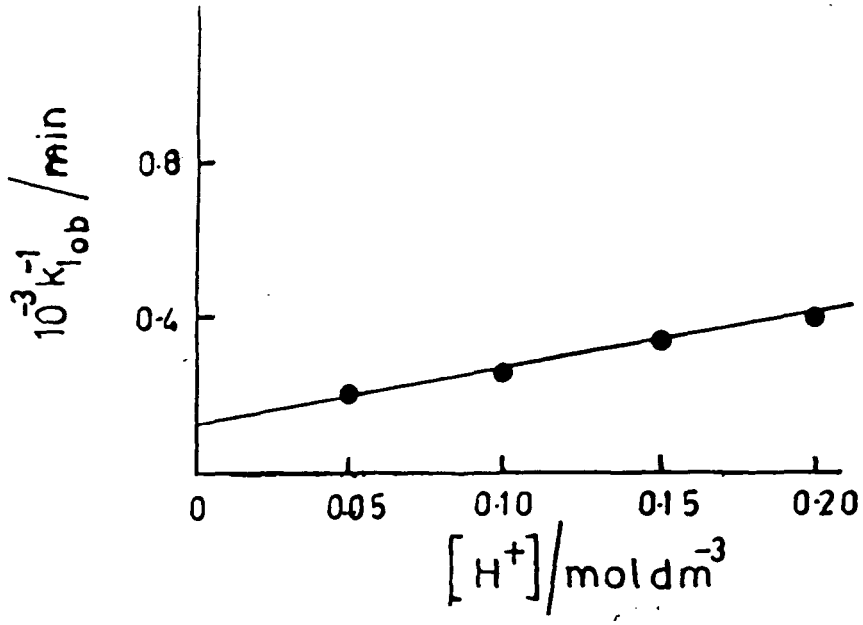


Figure 2c Plot of $1/k_{1ob}$ VS $[H^+]$ in the absence of SDS

Temp = 30°C, $[L]_o$ = 0·08 mol dm^{-3}, μ = 0·20 mol dm^{-3},

MnO_4^- = 2×10^{-4} mol dm^{-3}, [SDS] = Nil

equation (8) predicts a linear plot between $1/k_{lob}$ vs $1/[L]_o$ which is verified in figure 1.

(b) At constant lysine concentration using equation (6) the relation between k_{lob} and $[H^+]$ may be obtained.

$$k_{lob} = \frac{k_1^o [L]_o}{K_2[H^+] + K_{12}[H^+][L]_o + K_{212}[L]_o}$$

$$\frac{1}{k_{lob}} = \frac{K_2(1+K_1[L]_o)[H^+]}{k_1^o[L]_o} + \frac{K_{212}[L]_o}{k_1^o[L]_o}$$

$$= \frac{K_2(1+K_1[L]_o)[H^+]}{kK_2K_{12}[L]_o} + \frac{K_{212}}{kK_2K_{12}}$$

$$= \frac{(1+K_1[L]_o)}{kK_{12}[L]_o} .[H^+] + \frac{1}{k} \qquad .....(9)$$

equation (9) predict a linear plot between $1/k_{lob}$ vs $[H^+]$. This behaviour is verified by figure 2a. Furthermore, the reciprocal of the intercept of the above plot gives k and it is also observed that at different lysine concentration the plot $1/k_{lob}$ vs $[H^+]$ gives the same intercept (Fig. 2b, 2c) which give the average value of rate constant, k, $8.58 \times 10^{-3} min^{-1}$. A plot between $1/[L]_o$ and slope of the lines obtained from the above slope(9) at different lysine concentration is also found to be linear,

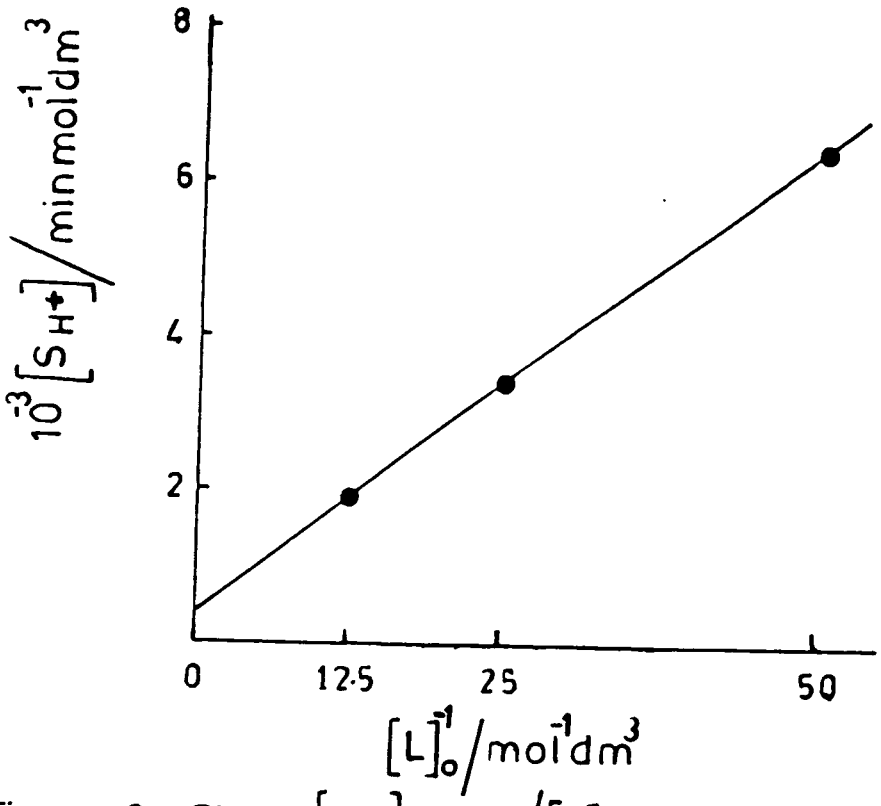


Figure 3 Plot of $[S_{H^+}]$ VS $1/[L]_o$ in the absence of SDS

$$\text{slope(9)} = 1/kK_{12}\,(1/[L]_o) + 1/kK_2 \qquad \ldots\ldots(9')$$

as shown in figure 3. Using the values of incercepts and slope of these lines K_1 and K_2 may be evaluated

$$\text{Intercept(9')} = \frac{1}{kK_2}$$

$$0.4\times10^{3} = \frac{1}{8.58\times10^{-3}\times K_2}$$

Therefore,

$$K_2 = \frac{1}{8.58\times10^{-3}\times0.4\times10^{3}}$$

$$K_2 = 0.29 \text{ mol dm}^{-3}$$

$$\text{slope(9')} = \frac{1}{kK_1K_2}$$

$$0.12\times10^{3} = \frac{1}{8.58\times10^{-3}\times0.29\times K_1}$$

Therefore,

$$K_1 = \frac{1}{8.58\times10^{-3}\times0.29\times0.12\times10^{3}}$$

$$K_1 = 3.3 \text{ mol}^{-1}\text{dm}^{3}$$

Evaluation of K_1, K_2 and k from equation (8) and (9).

Using the slope of equation (8) and the value of $k = 8.58 \times 10^{-3}\ min^{-1}$, we can get the value of K_{12} as,

$$slope(8) = \frac{[H^+]}{kK_{12}}$$

$$K_{12} = \frac{[H^+]}{k.\{slope(8)\}}$$

$$= \frac{0.2}{8.58 \times 10^{-3} \times 0.024 \times 10^3}$$

$$K_{12} = 0.97 \text{ number}$$

Using the slope of equation (8) and the values of k and K_{12} as above we can estimate the value K_1 and K_2 individually

$$slope = \frac{1 + K_1[L]_o}{kK_{12}[L]_o} \qquad \text{From figure 2a}$$

$$K_1 = \frac{[kK_{12}[L]_o(slope)-1]}{[L]_o}$$

putting the values of k, K_{12}, slope and $[L]_o$, we get

$$K_1 = \frac{8.58 \times 10^{-3} \times 0.97 \times 0.02 \times 6.4 \times 10^3 - 1}{0.02}$$

$$K_1 = 3.26\ mol^{-1}\ dm^3$$

Knowing $K_{12} = K_1K_2 = 0.97$ number

We can get K_2 as,

$$K_2 = \frac{K_1K_2}{K_1}$$

$$= \frac{0.97}{3.26}$$

$$K_2 = 0.30 \text{ mol dm}^{-3}$$

Similar calculation at lysine concentration 0.04M and 0.08M gives the value of K_1 as 3.29 mol^{-1} dm^3 and 3.15 $\text{mol}^{-1}\text{dm}^3$ respectively. Which gives average values of K_1 and K_2 as 3.23 mol^{-1} dm^3 and 0.30 mol dm^{-3} respectively and compares favourably with the values predicted using equation (9).

Mechanism and kinetics of phase two :

In appears that during the course of the reaction auto-catalytic effect plays an important role. We attribute this effect to manganese(II). It is envisaged that manganese(II) forms a complex with the reactive species produced by equilibria (3) and (4). This complex is fragmented into two different

species R_1 and R_2 which subsequently decomposes unimolecularly to give the final product. It is further assumed that the rates of decomposition of R_1 and R_2 are similar. The complete scheme for phase two may given as follows :

$$L + H^+ \longrightarrow LH^+$$

$$HP \longrightarrow P^- + H^+$$

$$LH^+ + P^- \overset{K_1}{\rightleftharpoons} LHP$$

$$LHP \overset{K_2}{\rightleftharpoons} LP^- + H^+$$

$$LP^- + Mn^{II} + P^- \overset{K_c}{\rightleftharpoons} LPMnP \qquad .....(10)$$

$$LPMnP \overset{K_d}{\rightleftharpoons} R_1 + R_2 \qquad .....(11)$$

$$R_1 \xrightarrow{k_{2b}} .....$$

$$R_2 \xrightarrow{k'_{2b}} .....$$

The following rate expression may be obtained for the above mechanism:

$$\text{rate} = k_{2b}[R_1] + k'_{2b}[R_2]$$

$$= (k_{2b} + k'_{2b})[R_1] \quad \text{(assuming rate of decomposition of two radicals to be similar)}$$

$$= 2k'_2[R_1]$$

$$= \sqrt{K_d}\, 2k'_2 [LPMnP]^{1/2}$$

$$= \sqrt{K_c K_d}\; 2k'_2 \sqrt{Mn}\sqrt{[LP^-]}\sqrt{[P^-]} \qquad .....(12)$$

The concentrations of $[LP^-]$ and $[P_T^-]$ are taken from earlier equation on the assumption that the fraction of permanganate present in the form of LPMnP is very low. Putting the values of $[LP^-]$ and $[P^-]$ concentration as,

$$[LP^-] = \frac{K_2K_{12}[L]_o[P_7]}{K_2[H^+]+K_2K_{12}[L]_o+K_{12}[H^+][L]_o}$$

and

$$[P^-] = \frac{[H^+]K_2K_{12}[L]_o[P_7]}{(K_2[H^+]+K_2K_{12}[L]_o+K_{12}[H^+][L]_o).K_{12}[L]_o}$$

in equation (12) we get,

$$\text{rate} = 2k_2^o\left(\frac{K_2K_{12}[L]_o[P_7]}{K_2[H^+]+K_2K_{12}[L]_o+K_{12}[H^+][L]_o}\right)^{1/2} X \left(\frac{[H^+]K_2[P_7]}{K_2[H^+]+K_2K_{12}[L]_o+K_{12}[H^+][L]_o}\right)^{1/2}$$

$$= \frac{2k_2^oK_2(K_{12}[L]_o)^{1/2}[H^+]^{1/2}.[P_7]}{(K_2[H^+]+K_2K_{12}[L]_o+K_{12}[H^+][L]_o)} \qquad \text{.....(13)}$$

$$= \frac{2k_2^o(K_{12}[L]_o)^{1/2}[H^+]^{1/2}.[P_7]}{([H^+] + K_{12}[L]_o+K_1[H^+][L]_o)} \qquad \text{.....(14)}$$

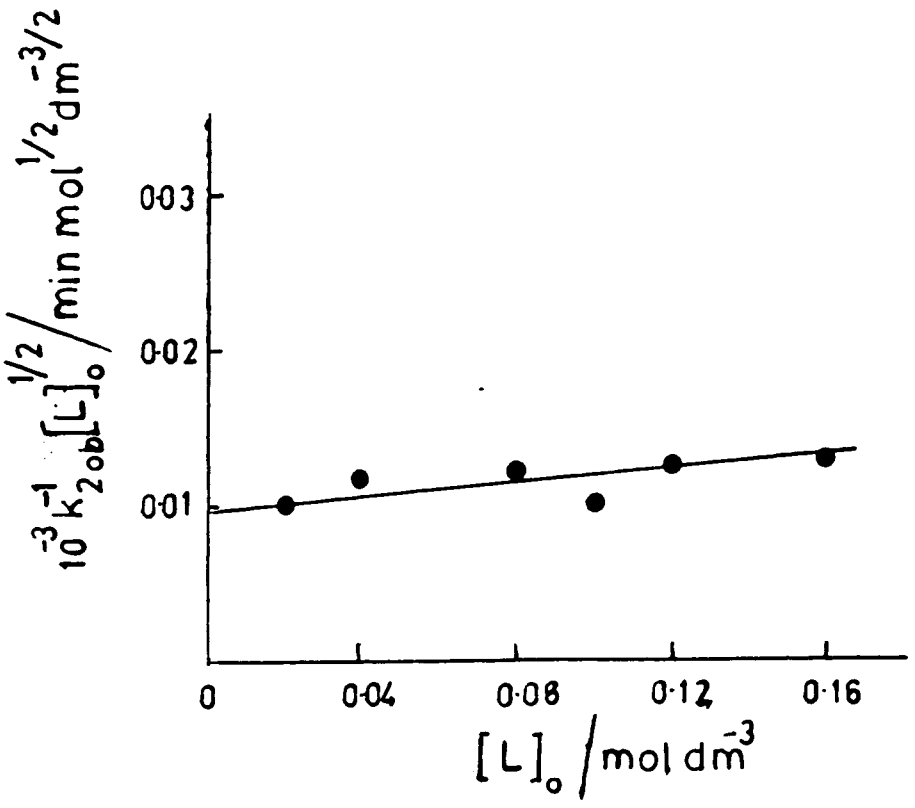


Figure 4 Plot of $[L]_o^{1/2}/k_{2ob}$ VS $[L]_o$ in the absence of SDS
Temp = 30°C $[H^+]$ = 0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3},
$[MnO_4^-] = 2 \times 10^{-4}$ mol dm^{-3}, [SDS] = Nil

(a) <u>At constant hydrogen ion concentration</u> :

The equation (14) may be rearranged to give,

$$\frac{k_{2ob}}{[L]_o^{1/2}} = \frac{k_2''}{[H^+] + (K_{12} + K_1[H^+])\,[L]_o}$$

$$\frac{[L]_o^{1/2}}{k_{2ob}} = \frac{[H^+]}{k_2''} + \frac{K_1(K_2+[H^+])[L]_o}{k_2''} \qquad .....(15)$$

where $k_2'' = 2k_2^o\, K_{12}^{1/2}\, [H^+]^{1/2}$

Equation (15) predicts that a plot between $[L]_o^{1/2}/k_{2ob}$ vs $[L]_o$ should be linear which is verified by figure 4. The intercept and slope of the above line are given as

$$\text{Intercept} = I_{15} = \frac{[H^+]^{1/2}}{2k_2^o\, K_{12}^{1/2}}$$

$$\text{Slope} = S_{15} = \frac{K_1^{1/2}(K_2+H^+)}{2k_2^o K_2^{1/2}[H^+]^{1/2}}$$

(b) <u>At constant lysine concentration</u> :

Equation (14) may be rearranged to give,

$$k_{2ob} = \frac{k_2'[H^+]^{1/2}[L]_o^{1/2}}{K_{12}[L]_o+(1+K_1[L]_o)[H^+]}$$

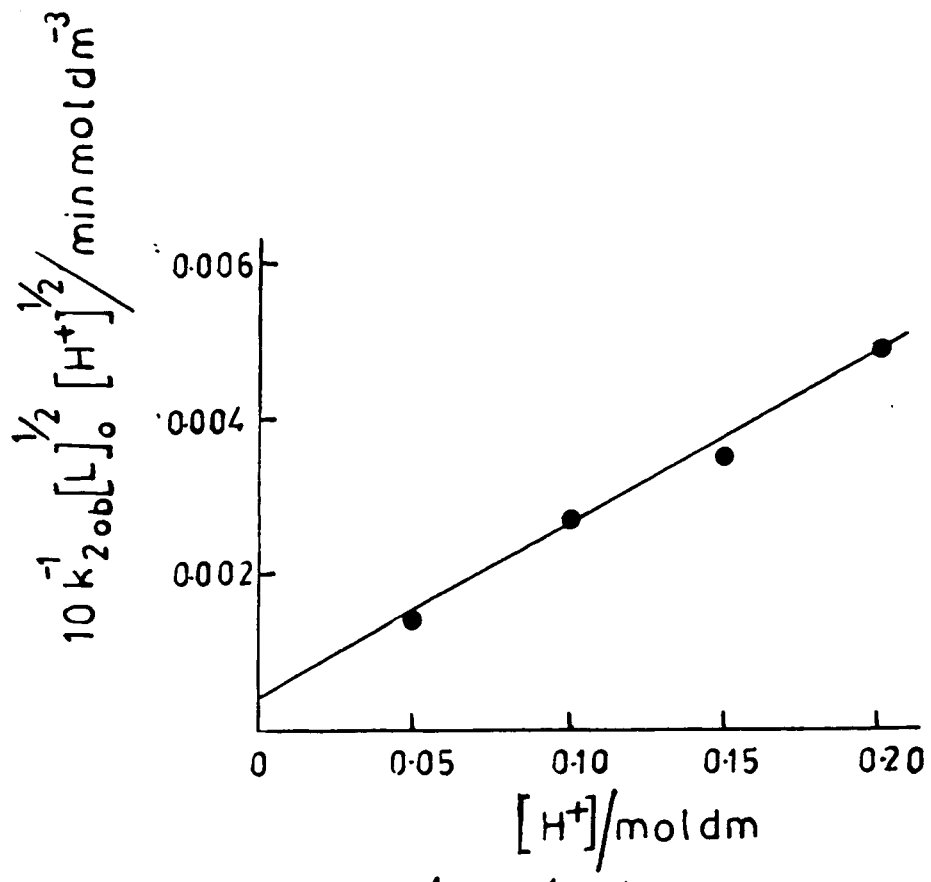


Figure 5a Plot of $[L]_o^{1/2}[H^+]^{1/2}/k_{2ob}$ VS $[H^+]$ in the absence of SDS

Temp = 30°C, $[L]_o$ = 0·02 mol dm^{-3}, μ = 0·20 mol dm^{-3}, $[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS] = Nil

or

$$\frac{k_{2ob}}{[H^+]^{1/2}[L]_o^{1/2}} = \frac{k_2'}{K_{12}[L]_o+(1+K_1[L]_o)[H^+]}$$

$$\frac{[L]_o^{1/2}[H^+]^{1/2}}{k_{2ob}} = \frac{K_{12}[L]_o}{2k_2^o K_{12}^{1/2}} + \frac{(1+K_1[L]_o[H^+]}{2k_2^o K_{12}^{1/2}}$$

$$= \frac{K_{12}^{1/2}[L]_o}{2k_2^o} + \frac{(1+K_1[L]_o)[H^+]}{2k_2^o K_{12}^{1/2}} \quad \ldots\ldots(16)$$

giving

$$\text{Intercept} = I_{16} = \frac{K_{12}^{1/2}[L]_o}{2k_2^o}$$

and

$$\text{Slope} = S_{16} = \frac{(1+K_1[L]_o)}{2k_2^o K_{12}^{1/2}}$$

The equation (16) predicts a linear graph between $[L]_o^{1/2}[H^+]^{1/2}/k_{2ob}$ vs $[H^+]$ with intercept and slope given above. This is verified by figure 5a. Using the values of K_1 and K_2 from data of phase one as found earlier the kinetic parameters of phase two have been evaluated. The intercept of equation (15) gives the values of k_2^o

$$\text{Intercept} = I_{15} = \frac{[H^+]^{1/2}}{2k_2^o \, K_{12}^{1/2}}$$

$$k_2^o = \frac{[H^+]^{1/2}}{I_{15} \cdot 2 \cdot K_{12}^{1/2}}$$

$$= \frac{(0.2)^{1/2}}{0.0095 \times 10^3 \times 2 \times (0.97)^{1/2}}$$

$$k_2^o = 2.4 \times 10^{-2} \text{ min}^{-1}$$

Using the value of k_2^o as estimated earlier and K_1 and K_2 from data of phase one. The slope and intercepts of equation (15) and (16) at different lysine concentration and $[H^+]$ have been evaluated and are found to be in good agreement with graphically determined values as shown below :

Prediction using equation (16) at different lysine concentration :

(a) At lysine concentration 0.02M

$$I_{16} = \frac{K_{12}^{1/2}[L]_o}{2k_2^o}$$

$$= \frac{0.98 \times 0.02}{2 \times 2.4 \times 10^{-2}} = 0.41$$

The graphical value is 0.40 (Fig. 5a).

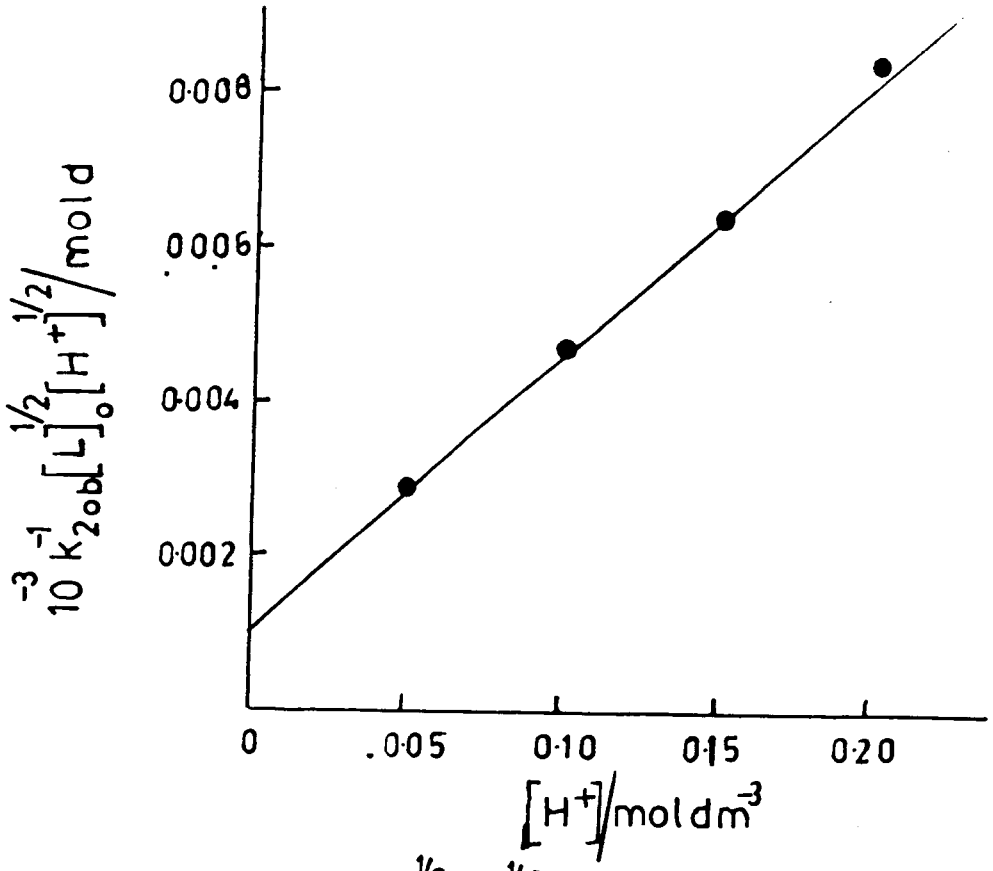


Figure 5b Plot of $[L]^{1/2}[H^+]^{1/2}/k_{2ob}$ VS $[H^+]$ in the absence of SDS

Temp = 30°C, $[L]_o$ = 0·04 mol dm^{-3}, μ = 0·20 mol dm^{-3}, $[MnO_4^-]$ = 2×10^{-4} mol dm^{-3}, [SDS] = Nil

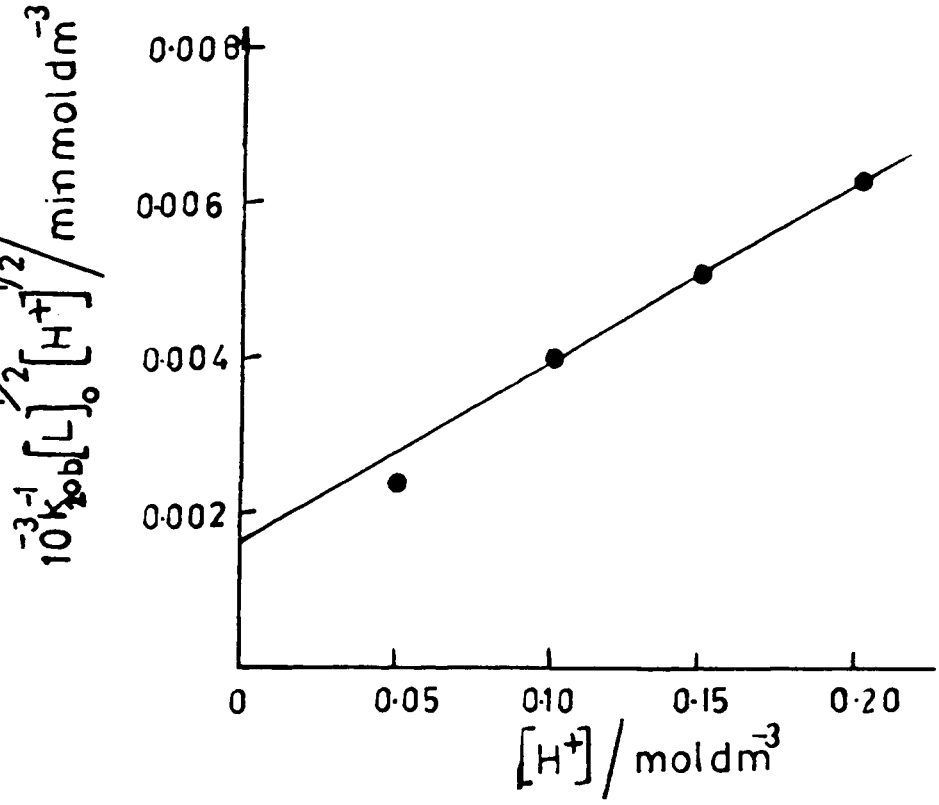


Figure 5c Plot of $[L]_o^{1/2}[H^+]^{1/2}/k_{2ob}$ VS $[H^+]$ in the absence of SDS

Temp = 30°C, $[L]_o$ = 0·08 mol dm^{-3}, μ = 0·20 mol dm^{-3}, $[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS] = Nil

(b) At lysine concentration 0.04M

$$I_{16} = \frac{0.98 \times 0.04}{2 \times 2.4 \times 10^{-2}} = 0.82$$

The graphical value is 1.0 (Fig. 5b).

(c) At lysine concentration 0.08M

$$I_{16} = \frac{0.98 \times 0.08}{2 \times 2.4 \times 10^{-2}} = 1.6$$

The graphical value is 1.6 (Fig. 5c).

(d) At lysine concentration 0.02M

$$S_{16} = \frac{1 + K_1[L]_o}{2k_2^o K_{12}^{1/2}}$$

$$= \frac{1 + 3.23 \times 0.02}{2 \times 2.4 \times 10^{-2} \times 0.98} = 22.6$$

The graphical value is 24 (Fig. 5a).

(e) At lysine concentration 0.04M

$$S_{16} = \frac{1+3.23 \times 0.04}{2 \times 2.4 \times 10^{-2} \times 0.98} = 24.0$$

The graphical value is 32 (Fig. 5b).

(f) At lysine concentration 0.08M

$$S_{16} = \frac{1+3.23 \times 0.08}{2 \times 2.4 \times 10^{-2} \times 0.98} = 26.8$$

The graphical value is 24.0 (Fig. 5c).

Prediction using equation (15) at different lysine concentration :

$$S_{15} = \frac{K_1^{1/2}(K_2 + H^+)}{2k_2^o K_2^{1/2} [H^+]^{1/2}}$$

$$= \frac{(3.23)^{1/2} (0.30 + 0.2)}{2x2.4x10^{-2}x(0.30)^{1/2}(0.2)^{1/2}}$$

$$= \frac{1.79 \times 0.50}{2x2.4x10^{-2}x0.548x0.447}$$

$$= 76.12$$

The graphical value is 30 (Fig. 4).

However, at other temperatures the slope of equation (15) does not compare favourably with the predicted values.

Oxidative degradation of lysine in the presence of surfactant

It is observed that in the first phase of the reaction the dependence of observed rate constant on different parameters in the presence of surfactant (k^s_{1ob}) does not change its behaviour as observed without surfactant. The plot $1/k^s_{1ob}$ vs $1/[L]_o$ is found to be linear and the plot between $1/k^s_{1ob}$ vs $[H^+]$ is also linear. However, a major difference is observed in the kinetic parameters of the second phase of the reaction. It may be recalled that a complex dependence on lysine and hydrogen ion concentrations of the rate constant in the second phase was observed. In the presence of surfactant the second phase observed rate constant (k^s_{2ob}) shows no variation with hydrogen ion concentration whereas the plot between $1/k^s_{2ob}$ vs $1/[L]_o$ is found to be linear. With this in view, the role of of surfactant appears to be quite different in respect of producing a new set of intermediates in the second phase whereas in the first phase the mechanism of the reaction is only marginally modified.

(a) Kinetics and mechanism of the reaction in the first phase:

Mechanism

$$L + H^+ \longrightarrow LH^+$$

$$HP \longrightarrow P^- + H^+$$

$$H^+ + (S_F)^{m-} \underset{}{\overset{K_H}{\rightleftharpoons}} (HS_F)^{(m-1)-}$$

$$LH^+ + (S_F)^{m-} \overset{K_{LS}}{\rightleftharpoons} L + (HS_F)^{(m-1)-}$$

$$LH^+ + P^- \overset{K_{LP}}{\rightleftharpoons} LHP$$

$$LHP + (S_F)^{m-} \xrightarrow{k_s} \ldots\ldots$$

Lysine is present in the protonated and deprotonated forms. The fraction of lysine complexed with Mn(VII) (i.e. P^-) is ignored.

Derivation of the rate expression :

From the above mechanism K_H, K_{LS} and K_{LP} may be defined as

$$K_H = \frac{[HS_F]^{(m-1)-}}{[H^+][S_F]^{m-}} \quad ; \quad K_{LS} = \frac{[L][HS_F]^{(m-1)-}}{[LH^+][S_F]^{m-}}$$

and

$$K_{LP} = \frac{[LHP]}{[LH^+]\,[P^-]}$$

The concentration of $[LH^+]$ may be obtained from the mass equation,

$$[L]_o = [LH^+] + [L]$$

and K_H, K_{LS} and K_{LP},

$$[L]_o = [LH^+] + [LH^+].[S_F]^{m-}K_{LS}/[HS_F]^{(m-1)-}$$

$$= [LH^+] (1 + K_{LS}/K_H.[H^+])$$

$$[LH^+] = K_H[L]_o[H^+]/K_H[H^+] + K_{LS}$$

The total manganese(VII) [i.e. P_7] is present in permanganate (i.e. P^-) and lysine-permanganate complex [i.e. LHP] forms

$$[P_7] = [P^-] + [LHP]$$

$$= \frac{[LHP]}{K_{LP}[LH^+]} + [LHP]$$

$$= \frac{[LHP]}{K_{LP}[LH^+]} (1 + K_{LP}[LH^+])$$

$$[LHP] = \frac{K_{LP}K_H[P_7][L]_o[H^+]}{K_H[H^+] + K_{LS} + K_{LP}K_H[L]_o[H^+]}$$

Using the above expression for the concentration of complex, LHP, the rate expression may be obtained as under:

$$\text{rate} = k_s[LHP].[S_F]^{m-}$$

$$\text{rate} = \frac{k_sK_{LP}K_H[P_7][L]_o[H^+][S_F]^{m-}}{K_H[H^+]+K_{LS}+K_{LP}K_H[L]_o[H^+]}$$

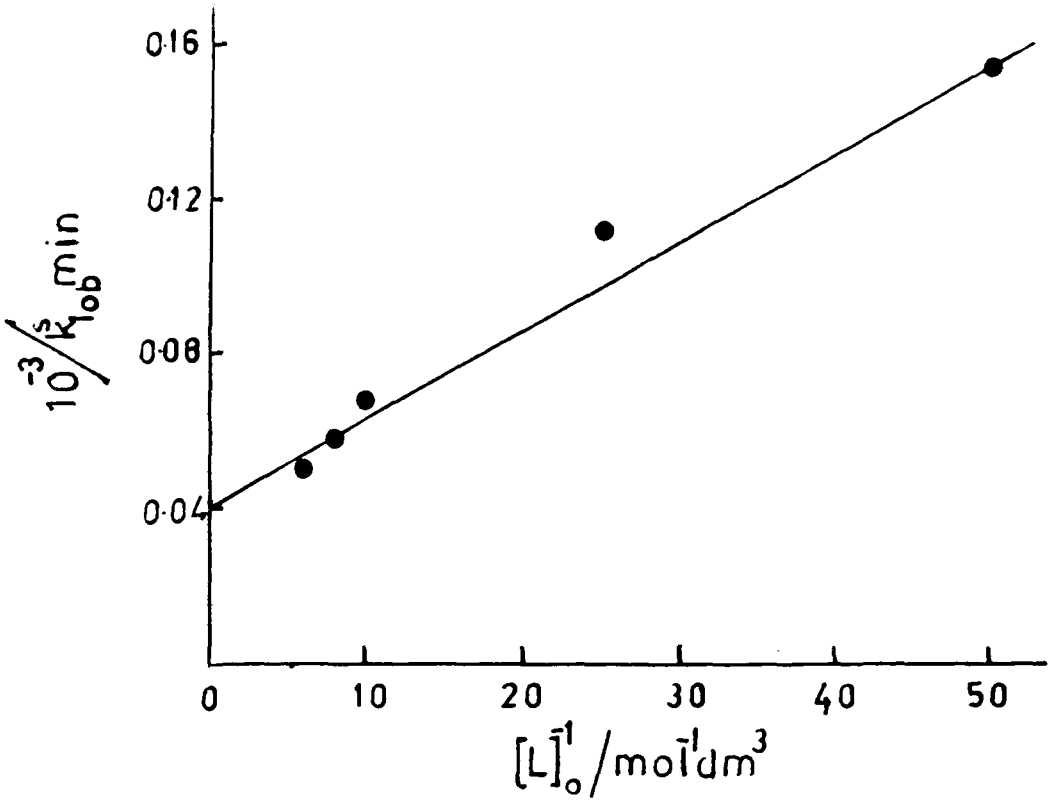


Figure 6 Plot of $1/k^s_{1ob}$ VS $1/[L]_o$ in the presence of SDS
Temp = 30°C, $[H^+]$ = 0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3},
$[MnO_4^-] = 2 \times 10^{-4}$ mol dm^{-3}, [SDS] = 0·01 mol dm^{-3}

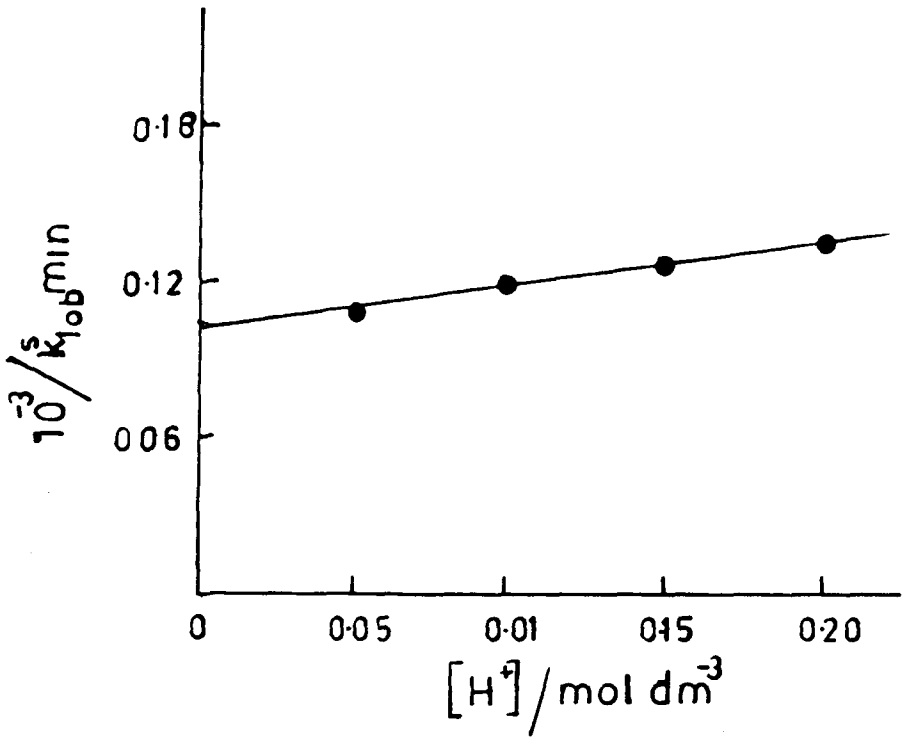


Figure 7a Plot of $1/k^{s}_{1ob}$ VS $[H^+]$ in the presence of SDS

Temp = 30°C , $[L]_o$ = 0·02 mol dm^{-3}, μ = 0·20 mol dm^{-3}

$[MnO_4^-]$ = 2X10^{-4} mol dm^{-3}, [SDS] = 0·01 mol dm^{-3}

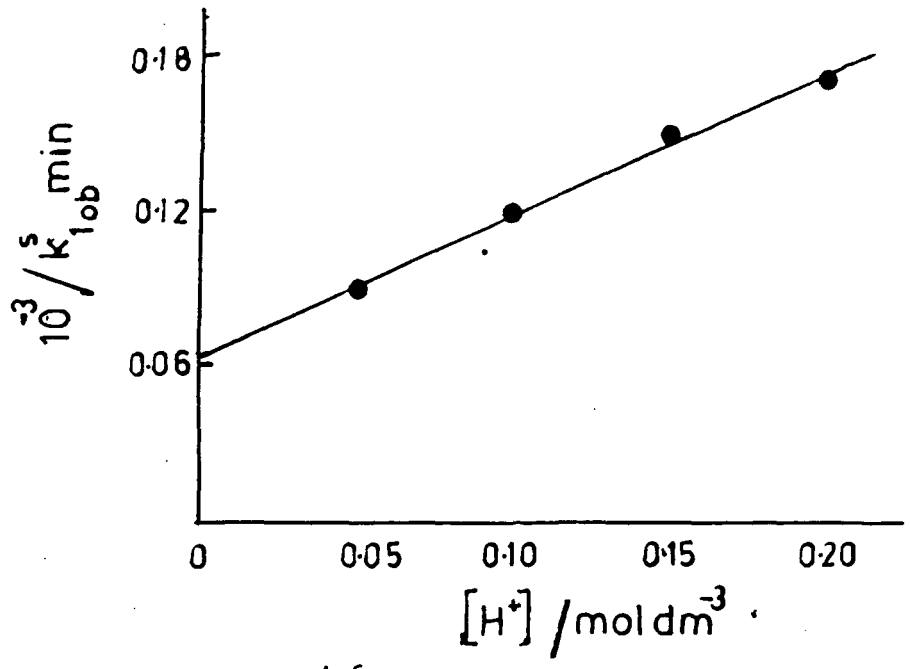


Figure 7b Plot of $1/k^{s}_{1ob}$ VS $[H^+]$ in the presence of SDS

Temp = 30°C $[L]_o$ = 0·04 mol dm^{-3}, μ = 0·20 mol dm^{-3}

$[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS] = 0·01 mol dm^{-3}

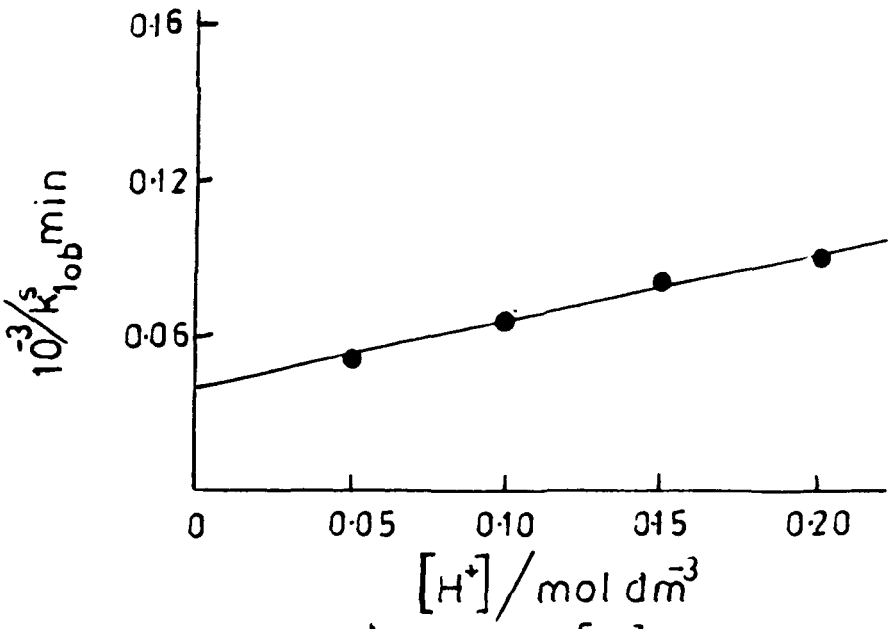


Figure 7c Plot of $1 / k^{s}_{1ob}$ VS $[H^+]$ in the presence of SDS

Temp = 30°C, $[L]_o$ = 0·08 mol dm^{-3}, μ = 0·20 mol dm^{-3},

$[MnO_4^-] = 2 \times 10^{-4}$ mol dm^{-3}, $[SDS]$ = 0·01 mol dm^{-3}

$$= \frac{k_s K_{LP}[HS_F]^{(m-1)-}[L]_o[P_7]}{K_H[H^+] + K_{LS} + K_{LP}K_H[L]_o[H^+]}$$

$$k^s_{lob} = \frac{k'_s[L]_o}{K_H[H^+] + K_{LS} + K_{LP}K_H[L]_o[H^+]} \qquad \ldots\ldots(17)$$

where

$$k'_s = k_s K_{LP}[HS_F]^{(m-1)-}$$

(a) At constant hydrogen ion concentration equation (17) gives,

$$\frac{1}{k^s_{lob}} = \frac{K_H[H^+]+K_{LS}}{k'_s} \cdot \frac{1}{[L]_o} + \frac{K_{LP}K_H[H^+]}{k'_s} \qquad \ldots\ldots(18)$$

equation (18) predicts a linear plot between $1/k^s_{lob}$ vs $1/[L]_o$ which is verified in figure 6.

(b) <u>At constant lysine concentration</u> :

Using equation (17) the relation between k^s_{lob} and $[H^+]$ may also be obtained,

$$\frac{1}{k^s_{lob}} = \frac{K_{LS}}{k'_s[L]_o} + \frac{K_H(1+K_{LP}[L]_o)}{k'_s[L]_o}[H^+] \qquad \ldots\ldots (19)$$

The equation (19) gives linear plot between $1/k^s_{lob}$ vs $[H^+]$. This behaviour is also verified by figures 7(a), (b) and (c).

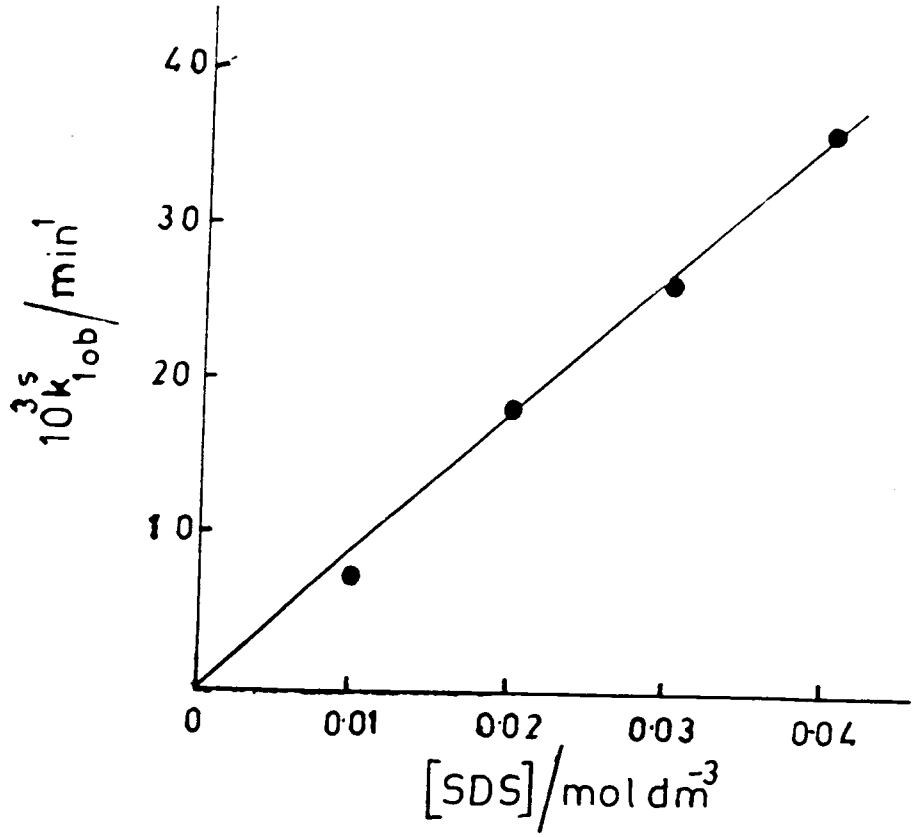


Figure 8 Plot of k^s_{1ob} VS SDS

Temp=30°C, $[H^+]$= 0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3}

$[MnO_4^-] = 2 \times 10^{-4}$ mol dm^{-3}, $[L]_o$ = 0·04 mol dm^{-3}

(c) At constant hydrogen ion and lysine concentration the relation between k^s_{lob} and [SDS] may be obtained as

$$k^s_{lob} = \frac{k_s K_{LP}[L]_o.[HS_F]^{(m-1)-}}{K_H[H^+]+K_{LS}+K_{LP}K_H[L]_o[H^+]}$$

$$= k'[SDS] \qquad .....(20)$$

The equation (20) predicts linear plot between k^s_{lob} vs [SDS]. This line passes through the origin as in figure 8.

Mechanism and kinetics of the reaction in the second phase

The most significant departure of kinetic feature of the reaction in the presence of the surfactant as compared to kinetic parameters observed without surfactant in the dependence of k^s_{2ob} on $[H^+]$. It appears that hydrogen ion does not play any role. The dependence of k^s_{2ob} on lysine concentration also indicates a complex formation of different nature. We have assigned the catalytic role in the second phase to manganese(II), which is the reaction product. It appears that the reactive species, LP^-, does not play any significant role in the presence of the surfactant but in its place a new manganese-lysine-permanganate complex plays a major role in the rate determining step. LP^- may be involved in producing the lysine manganese complex.

$$[LP^-] + Mn^{2+} \rightleftharpoons [LMnP]^+$$

with this in view, the mechanism of the phase two may be modified as under:

$$H^+ + (S_F)^{m-} \xrightleftharpoons{K_H} (HS_F)^{(m-1)-}$$

$$LH^+ + (S_F)^{m-} \xrightleftharpoons{K_{LS}} L + (HS_F)^{(m-1)-}$$

$$LH^+ + P^- \xrightleftharpoons{K_{LP}} LHP$$

$$LHP + Mn^{2+} \xrightleftharpoons{K_M} LMnP^+ + H^+$$

$$LMnP^+ + (S_F)^{m-} \xrightarrow{k_s} .....$$

Derivation of the rate expression :

The total manganese(VII) (i.e. P_7) is present in the form of three species P^-, LHP and lysine-manganese-permanganate complex [i.e. $(LMnP)^+$].

$$[P_7] = [P^-] + [LHP] + [LMnP]^+$$

$$= \frac{[LMnP]^+.[H^+]}{K_{LP}[LH^+].K_M Mn^{2+}} + \frac{[LMnP]^+[H^+]}{K_M.Mn^{2+}} + [LMnP]^+$$

$$= [LMnP]^+ \left(\frac{[H^+]+K_{LP}[LH^+][H^+]+K_{LP}K_M[LH^+]Mn^{2+}}{K_{LP}[LH^+]K_M Mn^{2+}}\right)$$

$$[LMnP]^+ = \frac{[P_7]K_{LP}[LH^+].K_M Mn^{2+}}{[H^+]+K_{LP}[H^+][LH^+]+K_{LP}K_M[LH^+]Mn^{2+}}$$

$$= \frac{[P_7]K_{LP}[LH^+]K_M.Mn^{2+}}{[H^+]+K_{LP}[H^+]\frac{[L]_oK_H[H^+]}{(K_H[H^+]+K_{LS})} + \frac{K_{LP}K_M[L]_oK_H[H^+]Mn^{2+}}{(K_H[H^+]+K_{LS})}}$$

$$= \frac{[P_7]K_{LP}K'_MK_H[L]_o[H^+]}{(K_H[H^+] + K_{LS})} \cdot \frac{(K_H[H^+] + K_S)}{[H^+](K_H[H^+]+K_{LS})+K_{LP}K_H[H^+]^2[L]_o+K_{LP}K'_MK_H[H^+][L]_o}$$

$$[LMnP]^+ = \frac{K_{LP}K'_MK_H[L]_o.[P_7]}{K_{LS}+K_{LP}K'_MK_H[L]_o}$$

Using the above expression for the concentration of complex, $[LMnP]^+$ the rate expression may be obtained as under:

$$\text{rate} = k_s[LMnP]^+[S_F]^{m-}$$

$$= \frac{k_sK_{LP}K'_MK_H[S_F]^{m-}[L]_o[P_7]}{K_{LS}+K_{LP}K'_MK_H[L]_o}$$

$$k^s_{2ob} = \frac{k_sK_{LP}.K'_MK_H[S_F]^{m-}[L]_o}{K_{LS}+K_{LP}K'_MK_H[L]_o}$$

$$= \frac{k_sk'[S_F]^{m-}[L]_o}{K_{LS} + k'[L]_o} \qquad \text{.....(21)}$$

where

$$k' = K_{LP}K'_MK_H$$

Using equation (21) under different experimental conditions the relationship between the observed rate constant,

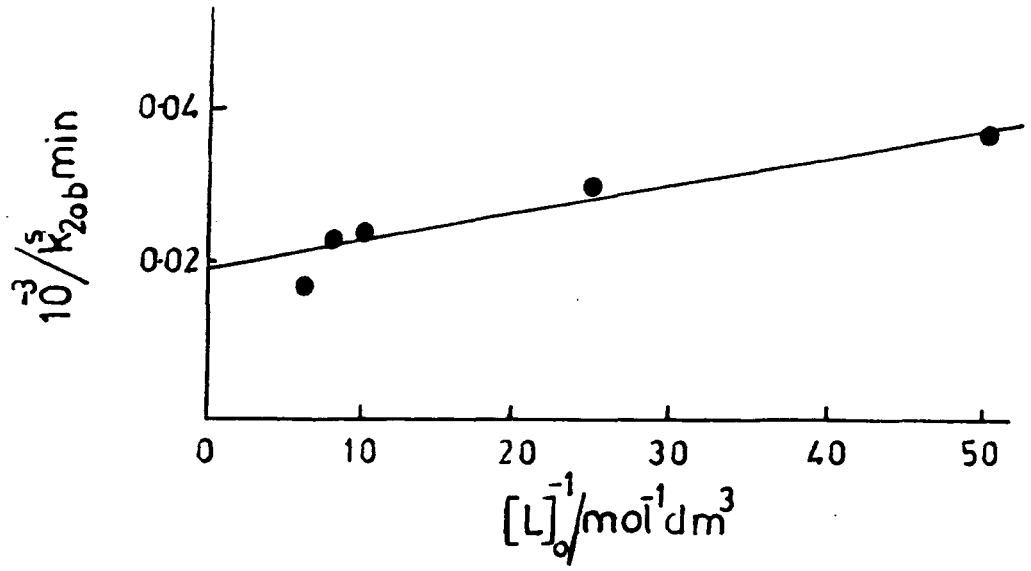


Figure 9 Plot of $1/k^{s}_{2ob}$ VS $1/[L]_o$ in the presence of SDS

Temp=30°C, $[H^+]$=0·20 mol dm^{-3}, μ=0·20 mol dm^{-3}

$[MnO_4^-]$=2X10^{-4} mol dm^{-3}, [SDS]=0·01 mol dm^{-3}

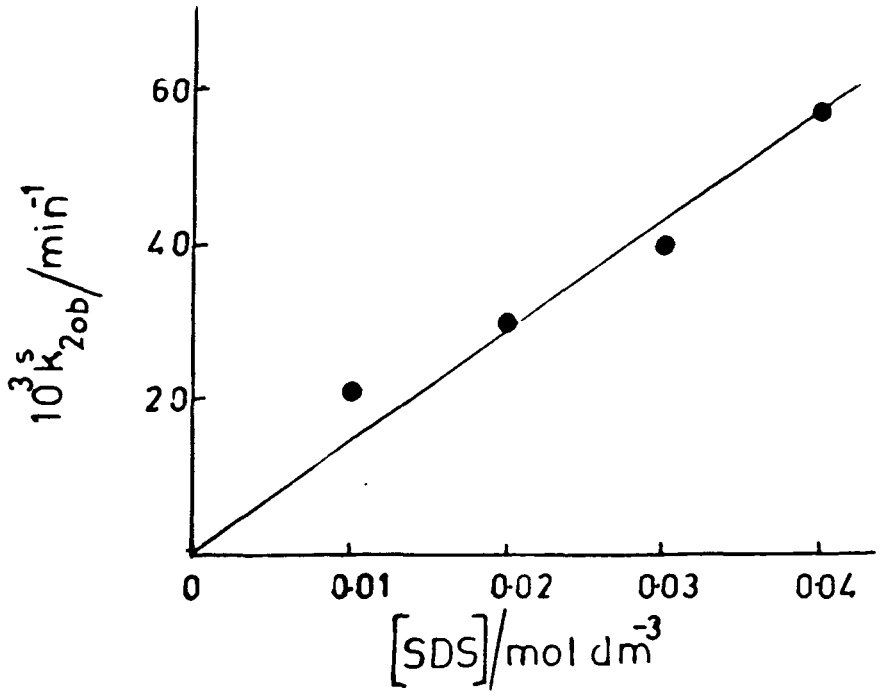


Figure 10 Plot of k^s_{2ob} VS SDS

Temp= 30°C, $[H^+]$ = 0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3},

$[MnO_4^-] = 2 \times 10^{-4}$ mol dm^{-3}, $[L]_o$ = 0·04 mol dm^{-3}

k^s_{2ob} and $[L]_o$ and relationship between k^s_{2ob} and $[H^+]$ may be expressed as follows :

(a) At constant hydrogen ion concentration equation (21) gives

$$\frac{1}{k^s_{2ob}} = \frac{K_{LS}}{k_s k'[S_F]^{m-}} \cdot \frac{1}{[L]_o} + \frac{1}{k_s[S_F]^{m-}} \qquad .....(22)$$

from equation (22) is predicted a linear plot between $1/k^s_{2ob}$ vs $1/[L]_o$ which is verified in figure 9.

(b) <u>At constant lysine concentration</u>

No effect of the hydrogen ion concentration is observed.

(c) At constant hydrogen ion and lysine concentration equation (21) gives the relationship between k^s_{2ob} and SDS.

$$k^s_{2ob} = \frac{k_s k'[L]_o}{K_{LS}+k'[L]_o}.[SDS] \qquad .....(23)$$

The equation (23) predicts linear plot between k^s_{2ob} vs [SDS]. This linear line passes through the origin and the behaviour is verified by figure 10.

Activation parameters :

Activation parameters of the reaction have been estimated using slopes and intercepts of equation 8, 9, 15 and 16. It has been assume that the product equilibrium constant K_{12} which is product of K_1 and K_2 does not change with temperature this assumption has been based on account of ionic species involved the said equilibrium,

$$[LH^+] + [P^-] \underset{}{\overset{K_{12}}{\rightleftharpoons}} [LP^-] + [H^+]$$

It is believed that since the interaction involves oppositevely charged species on the both side of the equilibrium therefore, the forward and backward processes would have relatively very small activation energies. At 30°C the value of $K_{12}(K_1 x K_2)$ has been estimated as 0.97 we have assumed the same value of at different temperatures. The values of k, K_2, K_1 and k_2^o are calculated in the following manner:

From the plot between $1/k_{lob}$ vs $1/[L]_o$ at different temperatures the values of k have been calculated using the slopes of equation (8).

$$(Slope_{30})_8 = \frac{[H^+]}{kK_{12}} \qquad \text{(equation 8)}$$

giving,

$$(k)_{30} = \frac{[H^+]}{(Slope_{30})K_{12}} \qquad \text{(From figure 11)}$$

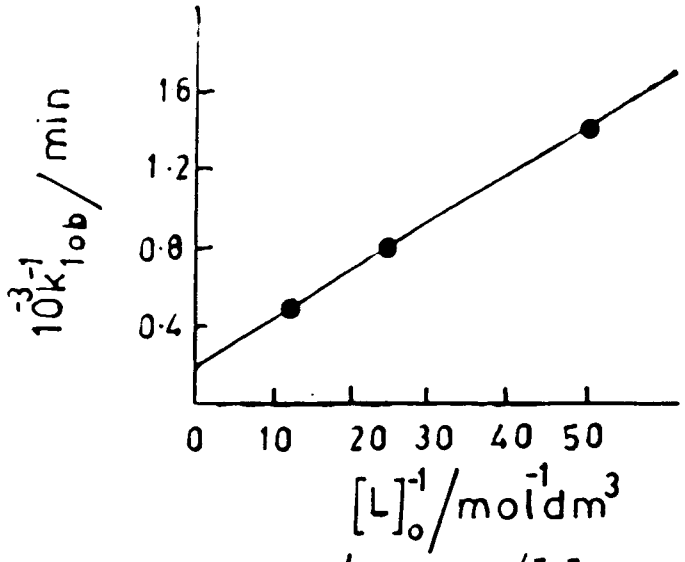


Figure 11 Plot of $1/k_{1ob}$ VS $1/[L]_o$ in absence of SDS
Temp = 30°C $[H^+]$ = 0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3}
$[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS] = Nil

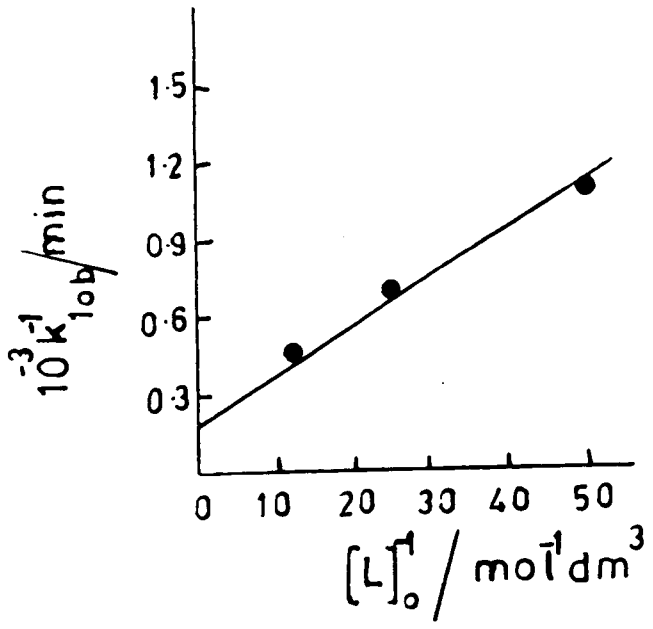


Figure 13 Plot of $1/k_{1ob}$ VS $1/[L]_o$ in the absence of SDS
Temp = 35°C, $[H^+]$ = 0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3},
$[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS] = Nil

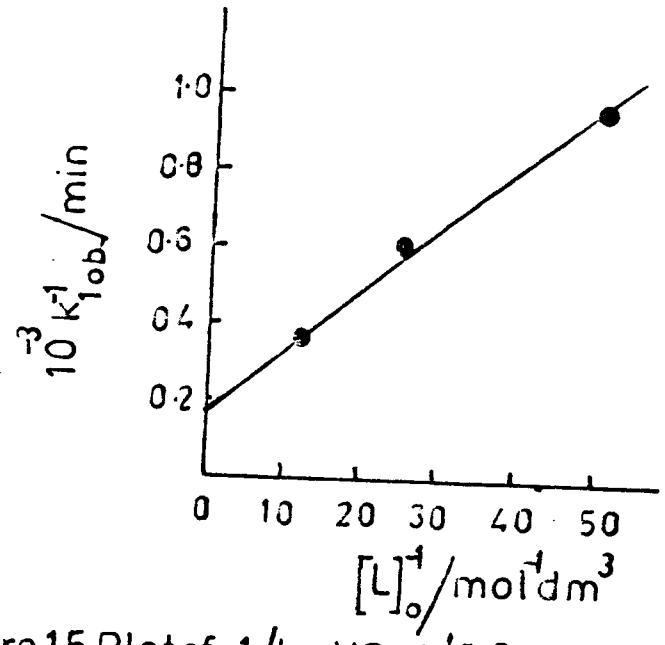


Figure 15 Plot of $1/k_{1ob}$ VS $1/[L]_o$ in the absence of SDS
Temp=40°C, $[H^+]$=0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3}
$[MnO_4^-] = 2 \times 10^{-4}$ mol dm^{-3}, [SDS] = Nil

$$= \frac{0.2}{0.024 \times 10^{3} \times 0.97}$$

$$(k)_{30} = 8.6 \times 10^{-3} \text{ min}^{-1}$$

Similarly,

$$(k)_{35} = \frac{0.2}{0.018 \times 10^{3} \times 0.97} \qquad \text{(From figure 13)}$$

$$= 11.5 \times 10^{-3} \text{ min}^{-1}$$

and

$$(k)_{40} = \frac{0.2}{0.014 \times 10^{-3} \times 0.97} \qquad \text{(From figure 15)}$$

$$= 14.7 \times 10^{-3} \text{ min}^{-1}$$

Using the intercept of equation (8) at different temperature the values of K_2 and K_1 may be obtained as under :

$$(\text{Int}_{30})_{8} = \frac{K_2 + [H^+]}{kK_2} \qquad \text{(From equation 8)}$$

$$(K_2)_{30} = \frac{[H^+]}{0.195 \times 10^{3} \times 8.6 \times 10^{-3} - 1} \qquad \text{(From figure 11)}$$

$$= \frac{0.2}{0.667}$$

$$(K_2)_{30} = 0.29 \text{ mol dm}^{-3}$$

but $K_{12} = 0.97$

$$(K_1)_{30} = \frac{0.97}{K_2}$$

$$= \frac{0.97}{0.29}$$

$$(K_1)_{30} = 3.3 \text{ mol}^{-1} \text{ dm}^3$$

Similarly,

$$(K_2)_{35} = \frac{0.2}{0.18\times10^{3}\times11.5\times10^{-3}-1} \quad \text{(From figure 13)}$$

$$= \frac{0.2}{1.061}$$

$$(K_2)_{35} = 0.19 \text{ mol dm}^{-3}$$

therefore,

$$K_{12} = 0.97$$

$$(K_1)_{35} = \frac{0.97}{0.19}$$

$$= 5.1 \text{ mol}^{-1} \text{ dm}^3$$

and

$$(K_2)_{40} = \frac{0.2}{0.16\times10^{3}\times14.7\times10^{-3}-1} \quad \text{(From figure 15)}$$

$$(K_2)_{40} = 0.15 \text{ mol dm}^{-3}$$

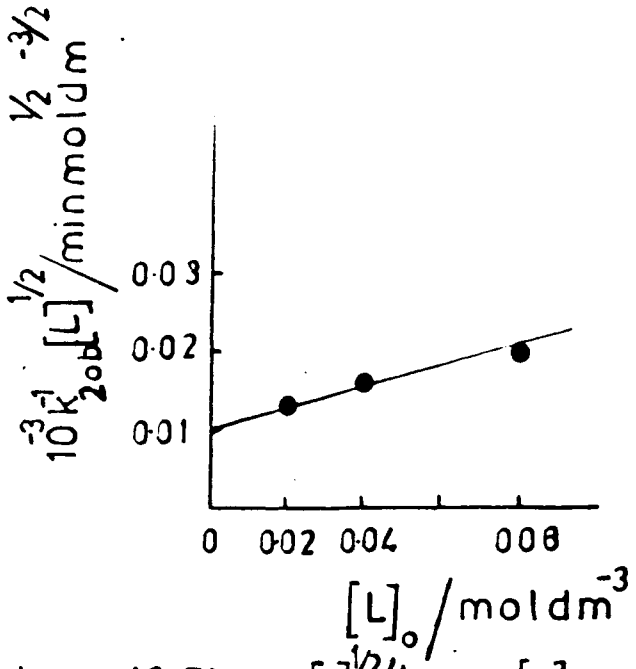


Figure 12 Plot of $[L]_o^{1/2}/k_{2ob}$ VS $[L]_o$ in the absence of the SDS

Temp = 30°C, $[H^+]$ = 0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3},

$[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS] = Nil

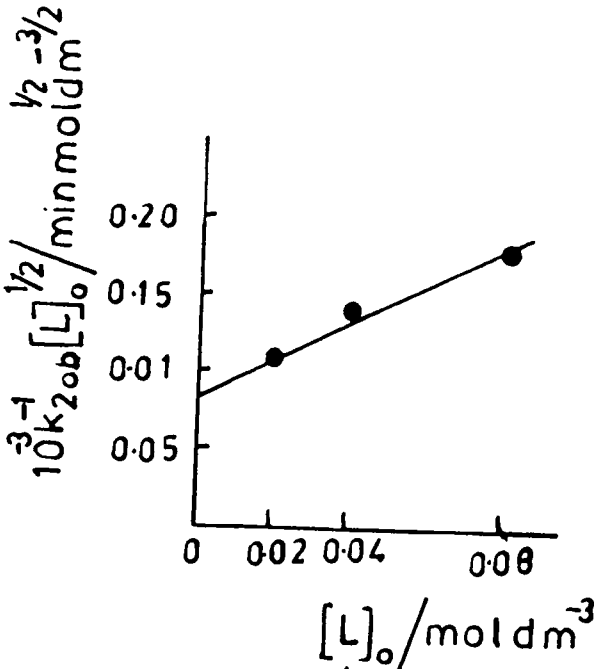


Figure 14 Plot of $[L]_o^{1/2}/k_{1ob}$ VS $[L]_o$ in the absence of SDS

Temp = 35°C, $[H^+]$ = 0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3}

$[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS] = Nil

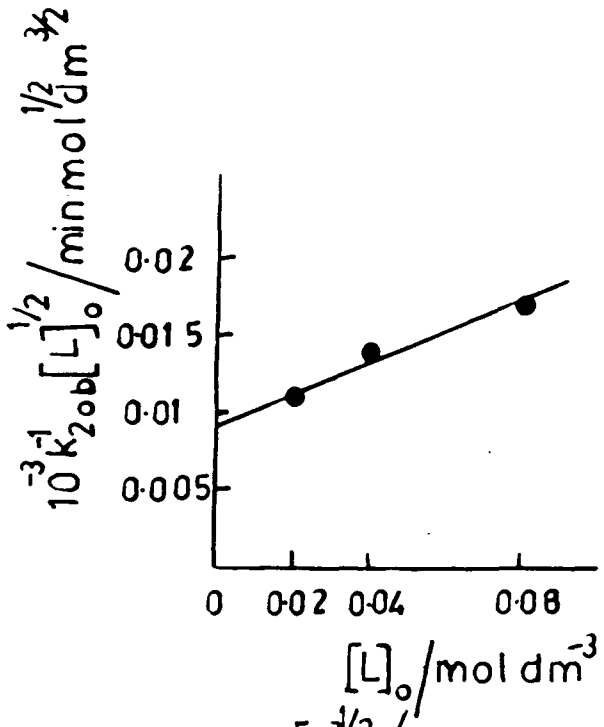


Figure16 Plot of $[L]_o^{1/2} / k_{2ob}$ VS $[L]_o$ in the absence of SDS
Temp=40°C, $[H^+]$=0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3},
$[MnO_4^-] = 2 \times 10^{-4}$ mol dm^3 [SDS] = Nil

therefore,

$$K_{12} = 0.97$$

$$(K_1)_{40} = \frac{0.97}{0.15}$$

$$= 6.5 \text{ mol}^{-1} \text{ dm}^3$$

From the intercepts of equation (15) at different temperature the values of k_2^o may be estimated as under:

$$(I_{30})_{15} = \frac{[H^+]^{1/2}}{k_2^o K_{12}^{1/2}} \qquad \text{(From figure 12)}$$

$$(k_2^o)_{30} = \frac{(0.2)^{1/2}}{0.0095 \times 10^3 \times (0.97)^{1/2}}$$

$$(k_2^o)_{30} = \frac{0.447}{0.0095 \times 10^3 \times 0.98}$$

$$(k_2^o)_{30} = 0.048 \text{ min}^{-1}$$

Similarly,

$$(k_2^o)_{35} = \frac{0.447}{0.008 \times 10^3 \times 0.98} \qquad \text{(From figure 14)}$$

$$(k_2^o)_{35} = 0.057 \text{ min}^{-1}$$

Therefore,

$$(k_2^o)_{40} = \frac{0.447}{0.0055 \times 10^3 \times 0.98} \qquad \text{(From figure 16)}$$

$$(k_2^o)_{40} = 0.082 \text{ min}^{-1}$$

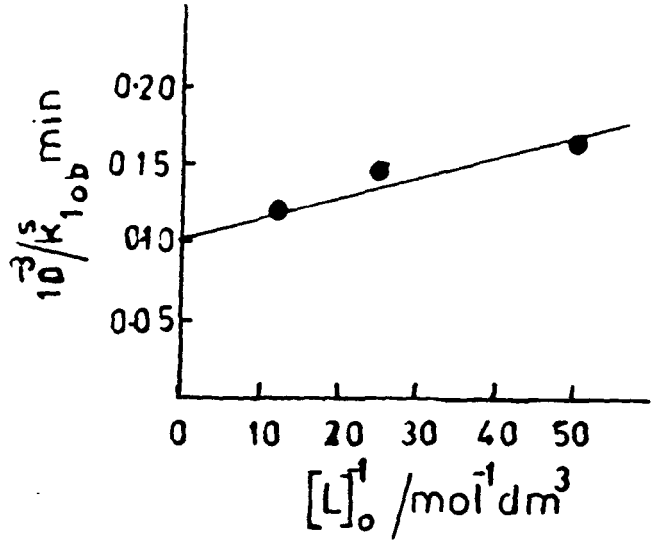


Figure 17 Plot of $1/k^{s}_{1ob}$ VS $1/[L]_o$ in the presence of SDS
Temp = 30°C, $[H^+]$ = 0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3},
$[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS] = 0·01 mol dm^{-3}

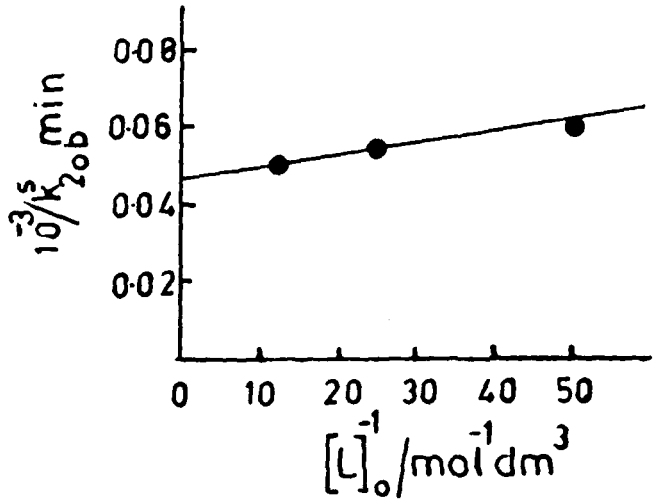


Figure 18 Plot of $1/k^{s}_{2ob}$ VS $1/[L]_o$ in the presence of SDS
Temp = 30°C, $[H^+]$ = 0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3},
$[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS] = 0·01 mol dm^{-3}

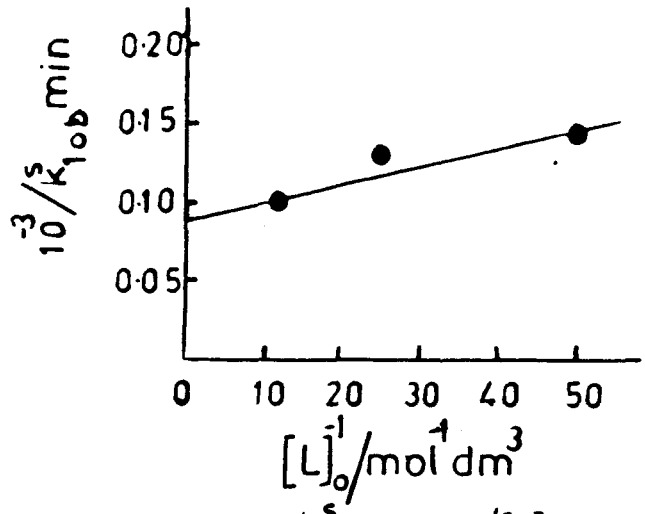


Figure 19 Plot of $1/k^s_{1ob}$ VS $1/[L]_o$ in the presene of SDS
Temp=35°C, $[H^+]$ 0·20 mol dm^{-3}, μ = 020 mol dm^{-3},
$[MnO_4^-]=2\times10^{-4}$ mol dm^{-3}, $[SDS]$ =0·01 mol dm^{-3}

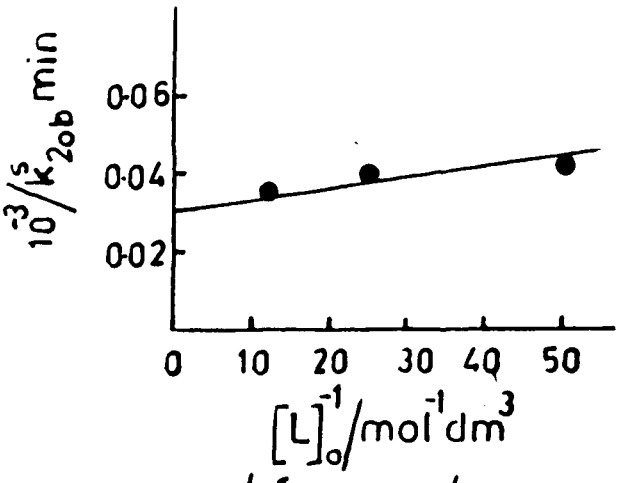


Figure 20 Plot of $1/k^s_{2ob}$ VS $1/[L]_o$ in the presence of SDS
Temp=35°C, $[H^+]$=0·20 mol dm^{-3}, μ=0·20 mol dm^{-3}
$[MnO_4^-]=2\times10^{-4}$ mol dm^{-3}, $[SDS]$ = 0·01 mol dm^{-3}

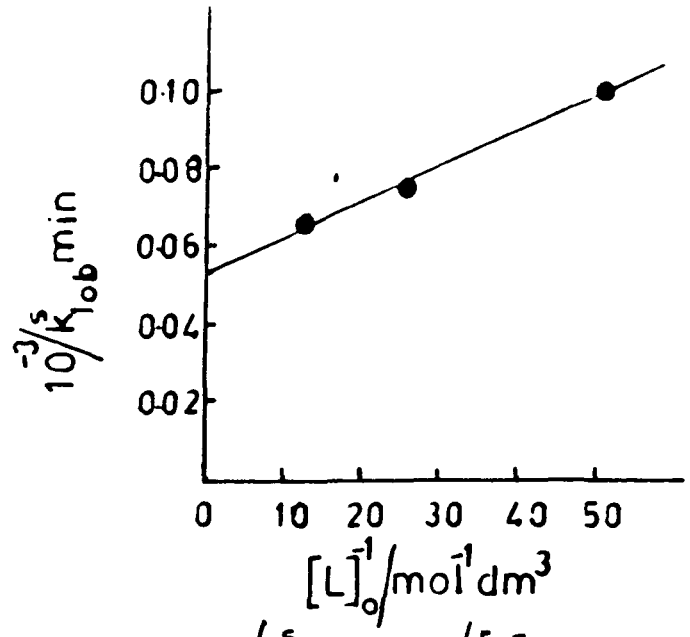


Figure 21 Plot of $1/k^s_{1ob}$ VS $1/[L]_o$ in the presence of SDS

Temp=40°C, $[H^+]$=0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3}

$[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS]=0·01 mol dm^{-3}

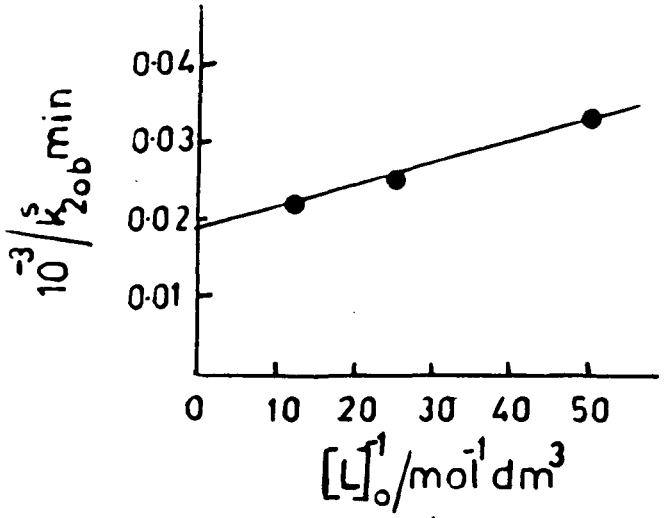
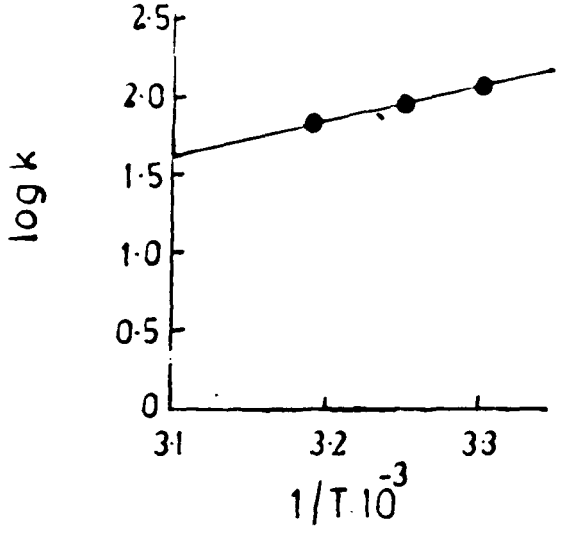


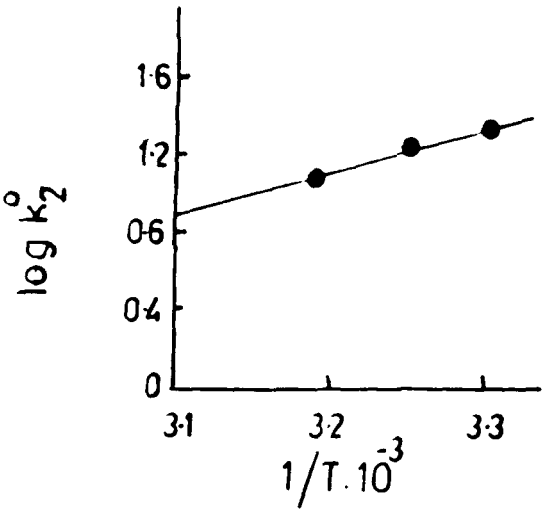
Figure 22 Plot of $1/k^s_{2ob}$ VS $1/[L]_o$ in the presence of SDS

Temp=40C, $[H^+]$=0·20 mol dm^{-3}, μ = 0·20 mol dm^{-3}

$[MnO_4^-]$ = 2 X 10^{-4} mol dm^{-3}, [SDS] = 0·02 mol dm^{-3}

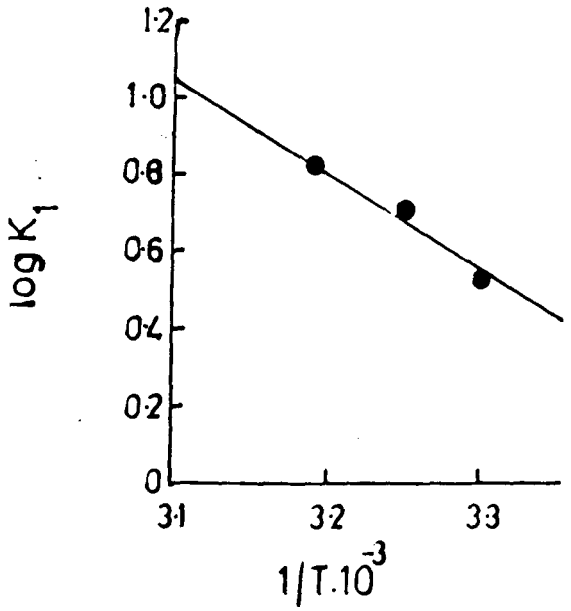


Plot of log k vs 1/T

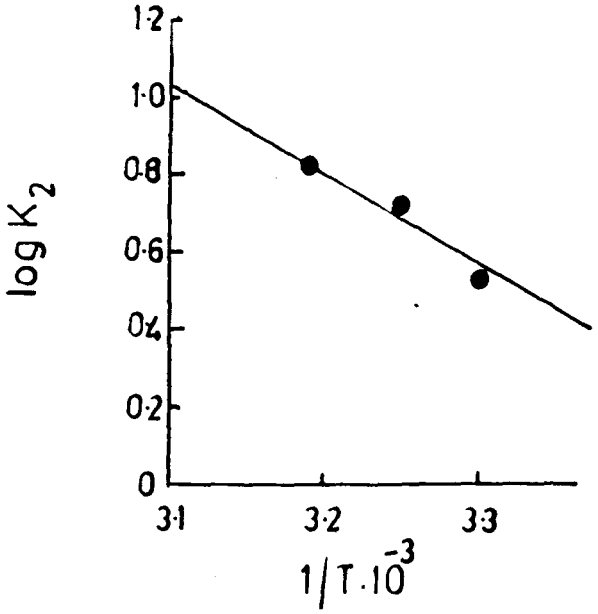


Plot of log k_2° vs 1/T

Figure 23



Plot of log K_1 vs 1/T



Plot of log K_2 vs 1/T

Figure 24

Arrhenius equation was used to evaluate activation energies of k, k_2^o [vide figure 23]. Similarly, the difference between the activation energy of forward and backward processes involved in the equilibria 1 and 2 were also estimated [vide figure 24]. The plots of $1/k^s_{lob}$ vs $1/[L]_o$ at different temperatures and found to be linear in the surfactant [vide figure 17 to 22]. However, the activation parameters for the rate constants in the presence of the surfactant could not be estimated because of lack of data.